

# Lesson 5

## Air Pollution

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## Table of Contents

Lesson 5: Air pollution.

5.1. Types and origin of air pollutants.

5.2. Effects of the air pollution.

5.3. Treatment of polluting gas emissions.

# Atmosphere

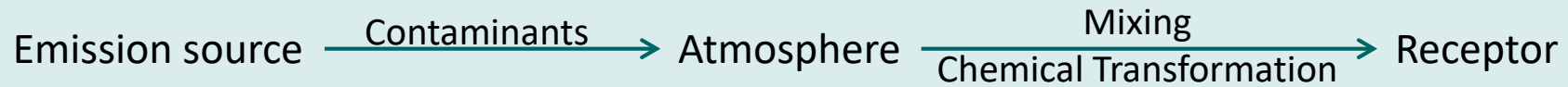
Structure and composition

Chemical Composition	
N <sub>2</sub>	78% (vol.)
O <sub>2</sub>	21% (vol.)
Ar	1% (vol.)
Noble Gases	He, Ne, Kr, Xe
Greenhouse gases	CH <sub>4</sub> , CO <sub>2</sub> , N <sub>2</sub> O, H <sub>2</sub> O <sub>(v)</sub>
Ozone	O <sub>3</sub>
Other gases	SO <sub>2</sub> , NO

# Atmosphere

Compound	Concentration (ppm)		Residence time (approx.)
	Clean atmosphere	Contaminated Atm.	
<b>Particles</b>	-	> 100 g/m <sup>3</sup>	
<b>CO</b>	120	1000 – 10000	65 days
<b>CO<sub>2</sub></b>	320000	400000	15 years
<b>SO<sub>2</sub></b>	0.2 – 10	20 – 200	40 days
<b>NO</b>	0.01 – 0.6	50 – 750	1 day
<b>NO<sub>2</sub></b>	0.1 – 1	50 – 250	1 day
<b>HNO<sub>2</sub></b>	0.001	1 – 8	
<b>HNO<sub>3</sub></b>	0.02 – 0.3	3 – 50	1 day
<b>O<sub>3</sub></b>	20 – 80	100 – 150	
<b>NH<sub>3</sub></b>	1 – 6	10 – 25	20 days
<b>CH<sub>4</sub></b>	1500	2500	8 – 10 years
<b>N<sub>2</sub>O</b>	300	-	10 – 150 years
<b>H<sub>2</sub>S</b>	0.2	-	-
<b>Pb</b>	5 · 10 <sup>-3</sup> mg/m <sup>3</sup>	0.5 – 3 mg/m <sup>3</sup>	-

## Air pollutants



**Emission:** contaminant concentration in the outlet of the source

**Immission:** contaminant concentration at ground level.

### Anthropogenic emission sources

- Transport
- Electric energy production
- Waste incineration
- Fuels (industrial and domestic use)
- Industrial activities

### Natural emission sources

- Volcanos
- Organic matter decomposition
- Erosion

**Primary Air Pollutants:** are emitted directly into the air from sources

**Secondary Air Pollutants:** chemicals formed through reactions in the atmosphere

## Air pollutants

Compounds	Primary air pollutants	Secondary air pollutants
Sulfur compounds	SO <sub>2</sub> , H <sub>2</sub> S	SO <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub> , MeSO <sub>4</sub>
Nitrogen compounds	NO, NH <sub>3</sub>	NO <sub>2</sub> , NO <sub>3</sub> <sup>-</sup> , MNO <sub>3</sub>
Organic carbon compounds	C1 – C3 Compounds	Aldehydes, ketones, acids
Carbon oxides	CO, CO <sub>2</sub>	none
Halogenated compounds	HF, HCl	none
Particles (ashes & aerosols)	Particles PM-10	-
Metals	Pb, Hg	-

### Units

#### volume/volume

ppm = cm<sup>3</sup>/m<sup>3</sup>

ppb = mm<sup>3</sup>/m<sup>3</sup>

#### mass/volume

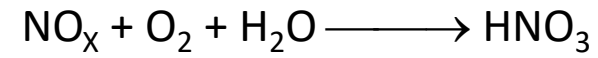
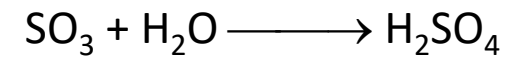
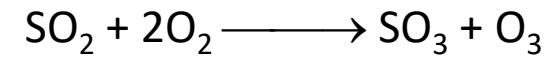
mg/m<sup>3</sup>

µg/m<sup>3</sup>

## Effects of air pollution

- Acid rain or acid deposition
- Photochemical smog
- Greenhouse effect and climate change
- Stratospheric ozone depletion

## Acid rain or acid deposition





## Acid rain or acid deposition

Living organisms

Forests

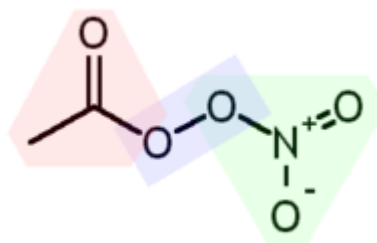
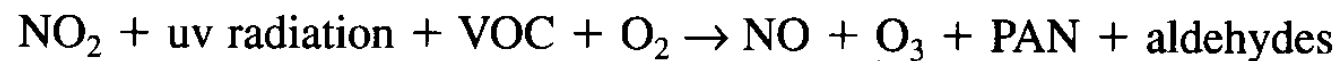
Buildings, statues

Lakes and rivers

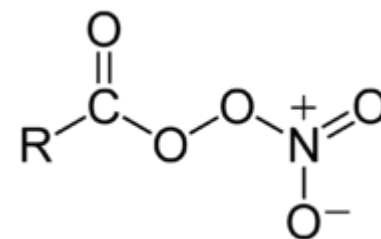
Soils and sediments

Release of Heavy metals like  
Al, Mn, Pb, Zn, Hg, Cd

## Photochemical smog



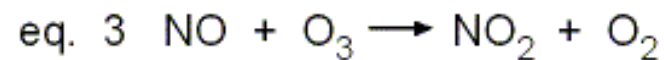
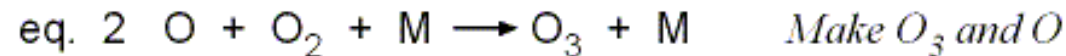
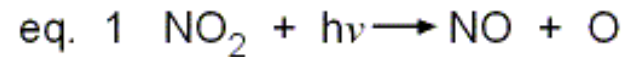
PAN  
Peroxyacetyl nitrate  
CH3COOONO2



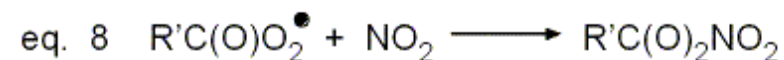
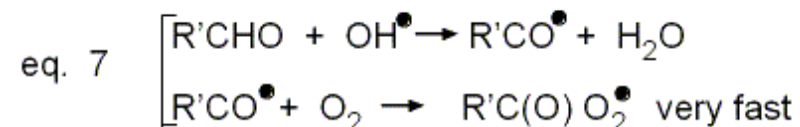
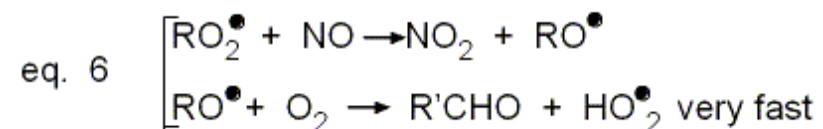
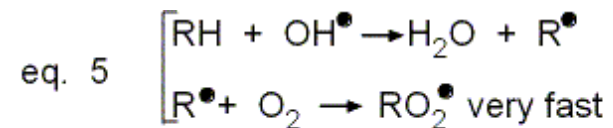
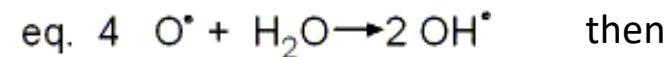
Peroxyacyl nitrate  
CxHyO3NO2

## Photochemical smog

### Generalized Reaction Scheme for Photochemical Smog Formation



This is a cyclic process that needs light and nitrogen oxides to generate oxygen atoms. Once formed, the oxygen atoms react with water to form hydroxyl radicals. The hydroxyl radicals then react with hydrocarbons according to equations 5 through 8 to form peroxyacyl nitrates (or PAN).



## Photochemical smog

### Generalized Reaction Scheme for Photochemical Smog Formation

In summary, this is what happens in photochemical smog formation

1. Nitrogen oxides generate oxygen atoms
2. Oxygen atoms form hydroxyl radicals
3. Hydroxyl radicals generate hydrocarbon radicals
4. Hydrocarbon radicals form hydrocarbon peroxides
5. Hydrocarbon peroxides form aldehydes
6. Aldehydes form aldehyde peroxides
7. Aldehyde peroxides form peroxyacyl nitrates

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$\text{RH} \rightarrow$  any hydrocarbon (i.e.  $\text{CH}_3\text{CH}_2\text{CH}_3$  or  $\text{CH}_3\text{CH}_3$ )

$\text{R}'\text{CHO} \rightarrow$  aldehyde  $\text{R}'-\text{C} \begin{array}{l} \text{=O} \\ \text{H} \end{array}$

$\text{R}'\text{CO}\cdot \longrightarrow$  acyl radical  $\text{R}'-\text{C} \begin{array}{l} \text{=O} \\ \cdot \end{array}$

$\text{R}'\text{C}(\text{O})\text{O}_2\cdot \longrightarrow$  acylperoxy radical  $\text{R}'-\text{C} \begin{array}{l} \text{=O} \\ \text{O}-\text{O}\cdot \end{array}$

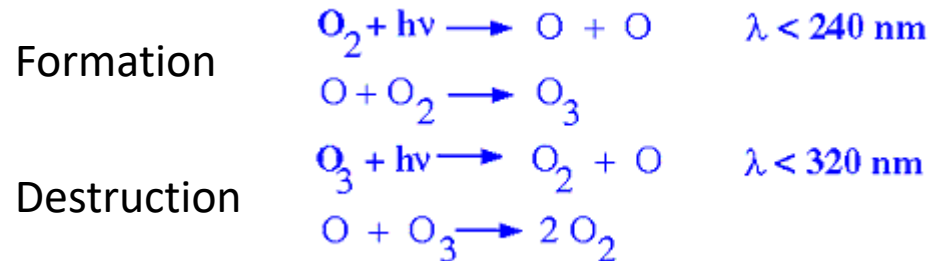
$\text{R}'\text{C}(\text{O})\text{O}_2\text{NO}_2 \longrightarrow$  acylperoxy nitrate  $\text{R}'-\text{C} \begin{array}{l} \text{=O} \\ \text{O}-\text{O}-\text{NO}_2 \end{array}$

When  $\text{R}'$  is a methyl group ( $-\text{CH}_3$ ) the substance is called PeroxyAcetyl Nitrate or PAN

## Stratospheric ozone depletion

Ozone protects from wavelengths (280–315 nm) of ultraviolet light (UV light)

### Ozone formation and destruction



- Natural process in the Stratosphere
- In equilibrium

### Ozone-depleting substances (ODS)

Prefix	Meaning	Atoms in the Molecule
CFC	chlorofluorocarbon	Cl, F, C
HCFC	hydrochlorofluorocarbon	H, Cl, F, C
HBFC	hydrobromofluorocarbon	H, Br, F, C
HFC	hydrofluorocarbon	H, F, C
PFC	perfluorocarbon	F, C
Halon	N/A	Br, Cl (in some but not all), F, H (in some but not all), C

## Stratospheric ozone depletion

Ozone can be destroyed by a number of free radical catalysts:

- hydroxyl radical ( $\text{OH}\cdot$ )
  - nitric oxide radical ( $\text{NO}\cdot$ )
  - atomic chlorine ion ( $\text{Cl}\cdot$ )
  - atomic bromine ion ( $\text{Br}\cdot$ )
- 

### $\text{Cl}\cdot$ radical formation and ozone depletion



Cyclic process

$\text{Cl}\cdot$  is not consumed

1. Cl atoms destroy ozone for about 2 years before they reached Troposphere where are stabilized as  $\text{HCl}$  or  $\text{ClONO}_2$ , and then removed from the atm.
2. Br is much more effective than Cl removing ozone but there is little Br in atm.
3. F is fast stabilized as  $\text{FH}$
4. Iodine reacts very fast in lower atm and do not reach Stratosphere

## Stratospheric ozone depletion

Ozone hole in North America during 1984 (abnormally warm reducing ozone depletion) and 1997 (abnormally cold resulting in increased seasonal depletion).

Image of the largest Antarctic ozone hole ever recorded (September 2006), over the Southern pole

## Greenhouse effect and climate change

Greenhouse Gases				Global Warming Potential
GHG	Pre-Industrial Conc.	2008 Conc.	Atmospheric lifetime	GWP (100 years)
Carbon dioxide (CO <sub>2</sub> )	278 ppm	365 ppm	50-200	1
Methane (CH <sub>4</sub> )	700 ppb	1745 ppb	12±3	25
Nitrous oxide (N <sub>2</sub> O)	270 ppb	314 ppb	120	298
Hydrofluorocarbons (HFCs)	0	14 ppt	1.5 – 209	150 – 14800 C <sub>2</sub> H <sub>4</sub> F <sub>2</sub> - CHF <sub>3</sub>
Perfluorocarbons (PFCs)	0	80 ppt	2600 – 50000	6500 – 9200 CF <sub>4</sub> – C <sub>2</sub> F <sub>6</sub>
Sulfur hexafluoride (SF <sub>6</sub> )	0	4.2 ppt	3200	23900

High GWP gases

CO<sub>2</sub>: fossil fuel combustion, land use change, cement production

CH<sub>4</sub>: Fossil fuels, rice paddies, waste dumps, livestock

N<sub>2</sub>O: Fertilizers, industrial processes, fossil fuel combustion

HFCs: Liquid coolants, alternative to ozone depleting substances

PFCs: refrigerant, semiconductor manufacturing, aluminum industry

SF<sub>6</sub>: electronic power transmission, magnesium and semiconductor industries



## Treatment of gas emissions

### Selection of the treatment based on gas properties

- Composition
- Flow
- Temperature
- Pressure
- Variability of composition, flow, temperature and pressure (start-up and shut-down)
- Explosive properties, flammable point...
- Corrosive properties

### Physicochemical properties

- Formula and molecular weight
- Boiling and melting points
- Solubility
- Absorption and adsorption properties
- Chemical behavior / reactivity
- Heat of absorption, condensation and solution
- Particle size distribution and density of the solid particles
- Odor threshold
- Health Effects
- pH
- Vapor pressure curve

## Treatment of gas emissions

### Contaminants in a gas emission

- VOC's
- Inorganic compounds
- Particles

### Technologies

- Particle separation units (gravity, centrifugation, ...)
- Incineration
- Condensation
- Filters
- Scrubbers
- Absorption units
- Adsorption units

Process	VOC's	Inorganic compounds	Particles
Incineration	X		
Adsorption	X		
Condensation	X		
Absorption	X	X	
Filtration		X	X
Electrostatic precipitator (ESP)			X
Scrubbers		X	X

## Treatment of gas emissions

Technology	Inlet concentration (ppm)	Efficiency
Condensation	>5.000	95+
	>2.500	90+
	>500	50+
Absorption	>5.000	99+
	>500	95+
	>200	90+
Adsorption	>5.000	99+
	>1.000	95+
	>200	90+
Thermal incineration	>100	99+
	>20	95+
Catalytic incineration	>100	95+
	>50	90+

Particle removal	Particle size ( $\mu\text{m}$ )	Efficiency
Gravitational settling chamber	>1600	95%, particles >300 $\mu\text{m}$
Cyclone	>10	80%, particles <20 $\mu\text{m}$
Spray scrubber	>3	98%, particles >5 $\mu\text{m}$
Filter	>0.5	95 – 99%, particles < 5 $\mu\text{m}$
Electrostatic precipitator (ESP)	>0.001	80 – 99%

## Gravitational settling chamber

Particles larger than about 50  $\mu\text{m}$

$d_p$  for 100% separation

$$d_p = \sqrt{\frac{18\mu_g u H}{\rho_p g L}}$$

$d_p$  = particle diameter (m)

$\rho_p$  = particle density ( $\text{kg/m}^3$ )

$\mu_g$  = gas viscosity ( $\text{kg/m s}$ )

$u$  = gas flow rate (m/s)

$H$  = chamber height (m)

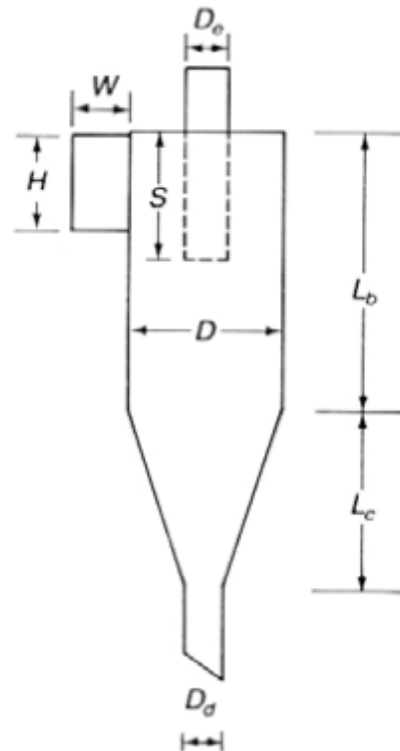
$L$  = chamber length (m)

$g$  = gravity ( $\text{m/s}^2$ )

## Cyclone separators

Particles larger than about  $1\ \mu\text{m}$

$d_p$  for 50% separation



$$d_{p,50} = \sqrt{\frac{9\mu H}{2\pi N V_t (\rho_p - \rho_g)}}$$

$$N = \frac{1}{H} \left( L_b + \frac{L_c}{2} \right)$$

$N$  = number of turns inside the device (no units)

$H$  = height of inlet duct (m or ft)

$L_b$  = length of cyclone body (m or ft)

$L_c$  = length (vertical) of cyclone cone (m or ft).

$V_t$  = terminal drift transverse velocity (m/s or ft/s)

$d_p$  = diameter of the particle (m or ft)

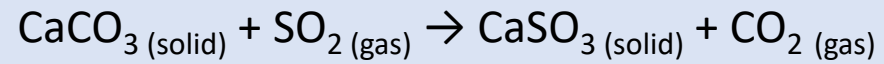
$\rho_p$  = density of the particle ( $\text{kg/m}^3$ )

$\rho_a$  = air density ( $\text{kg/m}^3$ )

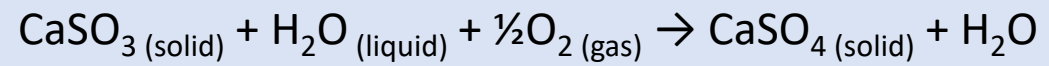
$\mu$  = air viscosity ( $\text{kg/m.s}$ ).

## Scrubbers

Flue-gas desulfurization

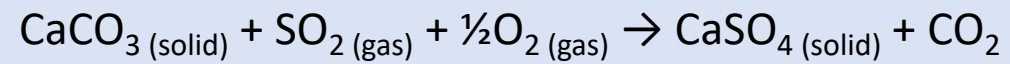


lime



Gypsum

Global reaction



## Catalytic conversion

### Contaminants

- Hydrocarbons (HC)
- Carbon monoxide (CO)
- Nitrogen oxides (NO<sub>x</sub>)

### Two-way (or "oxidation") catalytic converter

1. Oxidation of CO:  $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$
2. Oxidation of unburned hydrocarbons (HC):  
$$\text{C}_x\text{H}_{2x+2} + [(3x+1)/2] \text{O}_2 \rightarrow x\text{CO}_2 + (x+1) \text{H}_2\text{O}$$

### Three-way catalytic converters

1. Reduction of nitrogen oxides:  $2\text{NO}_x \rightarrow x\text{O}_2 + \text{N}_2$
2. Oxidation of CO
3. Oxidation of unburned hydrocarbons (HC)

## LESSON 5. AIR POLLUTION

1. a) The display of an atmospheric pollution control station shows an average daily concentration of ozone of  $20 \mu\text{g}/\text{m}^3$  at  $20^\circ\text{C}$  and 1 bar, ¿what is the ozone concentration in ppb? b) The exhaust gas from a truck contains 2.2 % (vol.) of CO ¿what is the concentration of CO in  $\text{mg}/\text{m}^3$  at  $30^\circ\text{C}$  and 1.02 atm.

Answer: 10.15 ppb, 25276  $\text{mg}/\text{m}^3$

2. A garage in a private house has the following dimensions: 4 m long, 4 m wide and 3 m high. The owner of the house parks his car in the garage and then closes the door. He remains in the car listening to some music with the engine running. If the IDLH (Immediately dangerous to life and health) of the CO is 1500 ppm; determine how long it will take to reach that value in the garage. Consider that the exhaust gas emission at idling speed is  $2.4 \text{ Nm}^3/\text{h}$ , and the CO concentration in the exhaust gas is  $8.7 \text{ g CO}/\text{Nm}^3$ . (Consider normal conditions for pressure and temperature)

Answer: 4.3 h

3. Limestone (calcium carbonate) is used to remove the sulfur dioxide produced at a coal thermal plant. The coal contains 3.0 wt. % of sulfur. The  $\text{SO}_2$  removal efficiency should be 90 %, in order to meet the legal environmental limits. Determine:

a) Stoichiometric mass (in kg) of calcium carbonate to remove 1 kg of S in the coal.

b) The mass (in kg) of limestone per ton of coal if 20 % excess of calcium carbonate is used. The concentration of calcium carbonate in the limestone is 85 %.

Answer: 2.81 kg  $\text{CaCO}_3/\text{kg S}$ , 119.118 kg limestone

4. In a wastewater treatment plant, the anaerobic digestion produces biogas: a mixture of methane and carbon dioxide. The methane can be burned to produce energy. A gaseous stream containing 80 % of  $\text{CH}_4$  (methane) and 20 % of  $\text{O}_2$  is burned with 200 % excess air. 80 % of the initial methane is transformed into  $\text{CO}_2$ , 10 % is transformed into CO, and the remaining 10 % is not burned. Determine:

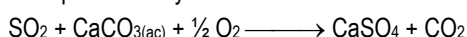
a) The volume of air used to burn 100 mol/h of methane, measured at 1 atm and  $25^\circ\text{C}$ .

b) The composition of the flue gas, on dry basis.

c) The amount of vapor of water generated per day

Answer: a)  $61.2 \text{ m}^3$ , b) 0.41 %  $\text{CH}_4$ , 0.41% CO, 3.26 %  $\text{CO}_2$ , 80.61 %  $\text{N}_2$ , 15.31 %  $\text{O}_2$ , c) 77.8 kg  $\text{H}_2\text{O}_{(\text{v})}/\text{gas}$

5. In an industrial plant, 30 t of a copper-nickel alloy is produced per day. Copper is obtained from sulfide minerals by roasting in a stream of air. In the roasting process, a contaminated gas stream ( $6.2 \cdot 10^4 \text{ Nm}^3$ ) with sulfur dioxide ( $1.5 \text{ g de SO}_2/\text{Nm}^3$ ) is produced. This gas is treated to reduce its  $\text{SO}_2$  content before its emission to the atmosphere. The gas is treated in a spray column with 60 % (wt.) calcium carbonate aqueous slurry:



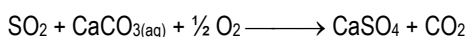
The exhaust gas from the spray column must contain as much as  $40 \text{ mg of SO}_2/\text{Nm}^3$  to comply with European regulations. Considering that the "purified gas" leaves the column at a molar flow rate of  $8.3 \cdot 10^7 \text{ mol/day}$ , determine:

a) Tons of  $\text{SO}_2$  removed per day

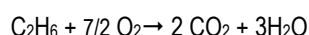
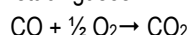
b) The amount of sludge (in t/day) generated and its composition (wt. %)

Answer: a) 2.72 t  $\text{SO}_2/\text{day}$ . b) 8.6 t sludge/day; 67.1 %  $\text{CaSO}_4$ ; 32.9 % water.

6. An industrial facility emits to the atmosphere  $2000 \text{ Nm}^3/\text{h}$  of stack gases with a composition of  $1000 \text{ mg}/\text{Nm}^3$  of  $\text{SO}_2$  and  $400 \text{ mg}/\text{Nm}^3$  of "CO + ethane" mixture. The emissions of  $\text{SO}_2$  to the atmosphere are removed by the addition of limestone (80% in  $\text{CaCO}_3$ ) to the furnace, thus, 90% of  $\text{SO}_2$  is removed as  $\text{CaSO}_4$ .



The emissions of "CO + ethane" mixture can be removed with a complete combustion of the stack gases. It requires the addition of  $480 \text{ mg de O}_2/\text{Nm}^3$  of stack gases.



Determine:

a) The daily consumption of limestone is kg

b) The composition of the mixture "CO + ethane" (expressed in molar %)

c) The volume of  $\text{CO}_2$  generated per day (expressed in normal conditions)

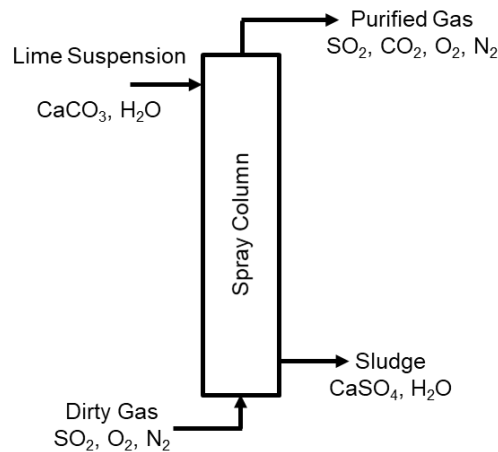
Answer: a) 84,38 kg/day; b) 18,80% CO, 81,19% ethane; c) 33126 L/day.



7. In a waste treatment facility, the wastes that are not biomethanized, are incinerated to obtain energy. 500 kg of waste with a high sulfur content are burned per day. The emissions derived from the combustion ( $500 \text{ Nm}^3/\text{kg}$  of incinerated waste) contain  $0.8 \text{ g/Nm}^3$  of  $\text{SO}_2$ . The maximum  $\text{SO}_2$  concentration in the gases is  $15 \text{ mg/Nm}^3$ . The gases are treated in a spray column with an aqueous suspension of  $\text{CaCO}_3$  at 60% wt. The calcium carbonate suspension is prepared from a limestone that contains 85% of  $\text{CaCO}_3$ . The efficiency of the spray adsorption column is 98%.

- Draw the sketch of the process with all the streams and available data.
- Determine the  $\text{SO}_2$  content (%) in the treated gas (the outlet stream of the spray column).
- Determine the consumption of limestone.
- Determine the height of a cylindrical tank, with 2 m in diameter, to store the calcium sulfate produced in 6 months. The density of the  $\text{CaSO}_4$  is  $2.3 \text{ kg/L}$ .

Answer: b)  $5,25 \cdot 10^{-4} \%$ ; c)  $360,29 \text{ kg/day}$ ; d)  $17,70 \text{ m}$ .



## ADDITIONAL EXERCISES (LESSON 5)

1. A laboratory is 10 m long, 5 m wide and 3 m high. There are 7 bottles of nitrogen containing 25 L at 200 atm. pressure. Due to a leak in the pipe, the bottles release all the nitrogen into the laboratory. Determine the percentage of O<sub>2</sub> in the lab when the 7 nitrogen bottles are empty. The O<sub>2</sub> threshold limit is 18 % in volume. Is there any risk for the people in the lab? The laboratory is at 1 atm and 25°C.

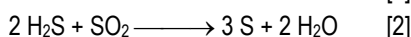
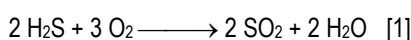
Answer: 17.03 % Danger

2. A gas flow of 930 Nm<sup>3</sup>/h flows through the chimney of a nitrogen fertilizer factory. This installation uses 20000 Nm<sup>3</sup>/day of natural gas with a density is 0.75 g/L (in normal conditions).

If the emission factor for nitrogen oxides is 3 kg NO<sub>x</sub>/t of natural gas, determine the concentration of NO and NO<sub>2</sub> in ppm (cm<sup>3</sup>/m<sup>3</sup>), if 90 % wt. of the NO<sub>x</sub> emission correspond to NO.

Answer: 1354.84 cm<sup>3</sup> NO/Nm<sup>3</sup>; 98.18 cm<sup>3</sup> NO<sub>2</sub>/Nm<sup>3</sup>.

3. The removal of the hydrogen sulfide (H<sub>2</sub>S) from a gas may be carried out by a process involving the reactions below, which ultimately lead to the production of elemental sulfur.



This method is used to remove the H<sub>2</sub>S from an exhaust gas that contains 3 % (wt.) of S. In the first reaction, 0.05 Nm<sup>3</sup> of air is used for each Nm<sup>3</sup> of gas, and the reaction takes place with an efficiency of 91 %. Then, the SO<sub>2</sub> generated in this first reaction is used in the second reaction. Determine:

a) The concentration of H<sub>2</sub>S in the gas.

B) The amount of elemental sulfur that can be obtained per Nm<sup>3</sup> of treated gas.

C) The amount of residual H<sub>2</sub>S or SO<sub>2</sub> remaining at the end of the process, expressed in mg/Nm<sup>3</sup> of gas.

DATA: Average gas density (in normal conditions) = 0.9 g / L

Answer: a) 0.844 mol SH<sub>2</sub>/Nm<sup>3</sup>, b) 26.88 g S/Nm<sup>3</sup> gas, c) 256 mg SO<sub>2</sub>/Nm<sup>3</sup> gas

4. 1500 kg/h of coal (88 % C, 4 % H, 4 % O, 1.28 % S, the rest are inert ashes) are burned with air. The air flow used is 20000 kg/h and the flue gas at 1 atm and 300 °C contain SO<sub>2</sub> at a concentration of 2450 mg/Nm<sup>3</sup>. Determine:

a) The flow rate of the flue gas expressed in m<sup>3</sup>/h.

b) The excess of oxygen used in percentage.

NOTE: Consider complete combustion of carbon.

Answer: 32887.7 m<sup>3</sup>; 17.7%

5. A gas stream contains 11% wt. of CO<sub>2</sub>. Other components of the gas stream are SO<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub>. This stream is passed through an absorber that only removes the CO<sub>2</sub> (gas sweetening). After the absorber, the CO<sub>2</sub> concentration decreases to 6.32% wt. The gaseous stream is then sent to an SO<sub>2</sub> absorber, the concentrations in the outlet stream from the SO<sub>2</sub> absorber are 11.88% SO<sub>2</sub> and 10.58% O<sub>2</sub>. Considering that 5 kg of CO<sub>2</sub> and 10 kg of SO<sub>2</sub> are absorbed per hour:

a) Draw a sketch of the process with all the available data.

b) Determine the mass flows in the outlet streams of the two absorbers.

c) Determine the SO<sub>2</sub> concentration in the outlet of the first absorber (CO<sub>2</sub> absorber)

d) Determine the composition of the inlet stream to the first absorber

Answer: a) 85.085 kg/h; b) 21,15%; c) 20,09% SO<sub>2</sub>, 8,99% O<sub>2</sub>; 59,92% N<sub>2</sub>.

6. An industry burns 100 t per day of coal with 4% sulfur. It generates 5500 Nm<sup>3</sup>/h of "flue gas" that contains SO<sub>2</sub>, NO<sub>x</sub> and other gases. The NO<sub>x</sub> emission factor is 1.8 kg NO<sub>x</sub>/t of carbon. The NO<sub>x</sub> contains 85% of nitrogen monoxide (NO) and 15% to nitrogen dioxide (NO<sub>2</sub>).

a) Determine the concentration of SO<sub>2</sub> in the "flue gas" before the purification process (in mg/Nm<sup>3</sup>).

b) Determine the concentration of NO and NO<sub>2</sub> in the "flue gas" before the purification process (in mg/Nm<sup>3</sup>).

c) The flue gas is treated and purified with a dry process using calcium carbonate, removing 97% of the SO<sub>2</sub>. Determine the mass (in t) of limestone (90% wt. content in calcium carbonate) consumed per day.

Answer: a) 60606 mg/m<sup>3</sup>; b) 1159 mg/m<sup>3</sup> NO, 204 mg/m<sup>3</sup> NO<sub>2</sub>; c) 13,47 t/day.

1. A laboratory is 10 m long, 5 m wide and 3 m high. There are 7 bottles of nitrogen containing 25 L at 200 atm. pressure. Due to a leak in the pipe, the bottles release all the nitrogen into the laboratory. Determine the percentage of O<sub>2</sub> in the lab when the 7 nitrogen bottles are empty. The O<sub>2</sub> threshold limit is 18 % in volume. Is there any risk for the people in the lab? The laboratory is at 1 atm and 25°C.

Answer: 17.03 % Danger

Volume of laboratory:  $10 \cdot 5 \cdot 3 = 150 \text{ m}^3$

Amount of O <sub>2</sub> at 1 atm and 25°C in the lab, in the beginning:	$150 \text{ m}^3 \cdot 0.21 = 31.5 \text{ m}^3 \text{ O}_2$	$n = \frac{P \cdot V}{R \cdot T} = \frac{1 \text{ atm} \cdot 31.5 \cdot 10^3 \text{ L}}{0.082 \frac{\text{atm} \cdot \text{L}}{\text{K} \cdot \text{mol}} \cdot 298.15 \text{ K}} = 1288.43 \text{ mol O}_2$
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Amount of N <sub>2</sub> at 1 atm and 25°C in the lab, in the beginning:	$150 \text{ m}^3 \cdot 0.79 = 118.5 \text{ m}^3 \text{ N}_2$	$n = \frac{P \cdot V}{R \cdot T} = \frac{1 \text{ atm} \cdot 118.5 \cdot 10^3 \text{ L}}{0.082 \frac{\text{atm} \cdot \text{L}}{\text{K} \cdot \text{mol}} \cdot 298.15 \text{ K}} = 4846.96 \text{ mol N}_2$
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Amount of N <sub>2</sub> released into the lab (7 bottles of 25 L at 200 atm)	$7 \cdot 25 \text{ L} = 175 \text{ L N}_2$	$n = \frac{P \cdot V}{R \cdot T} = \frac{200 \text{ atm} \cdot 175 \text{ L}}{0.082 \frac{\text{atm} \cdot \text{L}}{\text{K} \cdot \text{mol}} \cdot 298.15 \text{ K}} = 1431.59 \text{ mol N}_2$
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O <sub>2</sub> concentration in the lab, at the end:	$\frac{1288.43 \text{ mol O}_2}{(1288.43 + 4846.96 + 1431.59) \text{ mol (O}_2 + \text{N}_2)} \cdot 100 = 17.03\% \text{ O}_2$	< 18% Peligro
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2. A gas flow of 930 Nm<sup>3</sup>/h flows through the chimney of a nitrogen fertilizer factory. This installation uses 20000 Nm<sup>3</sup>/day of natural gas with a density is 0.75 g/L (in normal conditions).

If the emission factor for nitrogen oxides is 3 kg NO<sub>x</sub>/t of natural gas, determine the concentration of NO and NO<sub>2</sub> in ppm (cm<sup>3</sup>/m<sup>3</sup>), if 90 % wt. of the NO<sub>x</sub> emission correspond to NO.

*Answer: 1354.84 cm<sup>3</sup> NO/Nm<sup>3</sup>; 98.18 cm<sup>3</sup> NO<sub>2</sub>/Nm<sup>3</sup>.*

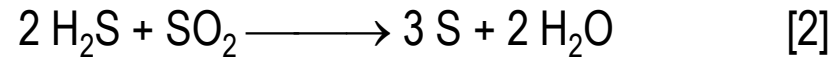
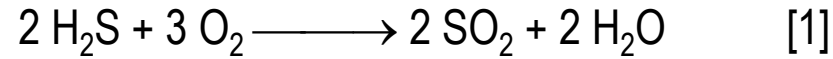
Production of NO<sub>x</sub>

$$\frac{20000 \text{ m}^3 \text{ natural gas}}{\text{day}} \cdot \frac{1 \text{ day}}{24 \text{ h}} \cdot \frac{0.75 \text{ g natural gas}}{1 \text{ L natural gas}} \cdot \frac{10^3 \text{ L}}{1 \text{ m}^3} \cdot \frac{1 \text{ t}}{10^6 \text{ g}} \cdot \frac{3 \text{ kg NO}_x}{1 \text{ t natural gas}} = 1.875 \text{ kg NO}_x/\text{h}$$

$$1.875 \text{ kg NO}_x/\text{h} \left\{ \begin{array}{l} \text{NO} \quad \frac{1.875 \text{ kg NO}_x}{\text{h}} \cdot 0.90 = 1.6875 \text{ kg NO/h} \\ \text{NO}_2 \quad \frac{1.875 \text{ kg NO}_x}{\text{h}} \cdot 0.10 = 0.1875 \text{ kg NO}_2/\text{h} \end{array} \right.$$

$$\left\{ \begin{array}{l} \text{NO} \quad \frac{1.6875 \text{ kg NO}}{\text{h}} \cdot \frac{1 \text{ h}}{930 \text{ m}^3} \cdot \frac{1 \text{ mol NO}}{30 \cdot 10^{-3} \text{ kg NO}} \cdot \frac{22.4 \cdot 10^3 \text{ cm}^3}{1 \text{ mol NO}} = 1354.84 \text{ cm}^3 \text{ NO/m}^3 \\ \text{NO}_2 \quad \frac{0.1875 \text{ kg NO}_2}{\text{h}} \cdot \frac{1 \text{ h}}{930 \text{ m}^3} \cdot \frac{1 \text{ mol NO}_2}{46 \cdot 10^{-3} \text{ kg NO}_2} \cdot \frac{22.4 \cdot 10^3 \text{ cm}^3}{1 \text{ mol NO}_2} = 98.18 \text{ cm}^3 \text{ NO}_2/\text{m}^3 \end{array} \right.$$

3. The removal of the hydrogen sulfide ( $\text{H}_2\text{S}$ ) from a gas may be carried out by a process involving the reactions below, which ultimately lead to the production of elemental sulfur.

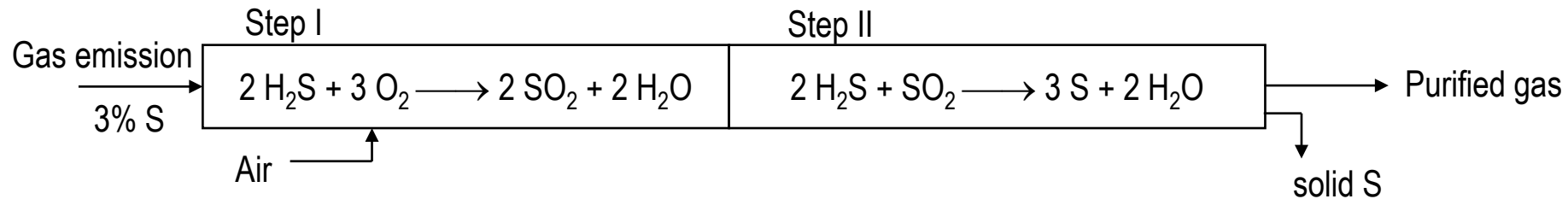


This method is used to remove the  $\text{H}_2\text{S}$  from an exhaust gas that contains 3 % (wt.) of S. In the first reaction, 0.05  $\text{Nm}^3$  of air is used for each  $\text{Nm}^3$  of gas, and the reaction takes place with an efficiency of 91 %. Then, the  $\text{SO}_2$  generated in this first reaction is used in the second reaction. Determine:

- The concentration of  $\text{H}_2\text{S}$  in the gas.
- The amount of elemental sulfur that can be obtained per  $\text{Nm}^3$  of treated gas.
- The amount of residual  $\text{H}_2\text{S}$  or  $\text{SO}_2$  remaining at the end of the process, expressed in  $\text{mg}/\text{Nm}^3$  of gas.

DATA: Average gas density (in normal conditions) = 0.9 g / L

Answer: a) 0.8438 mol  $\text{SH}_2/\text{Nm}^3$ , b) 26.85 g S/ $\text{Nm}^3$  gas, c) 300 mg  $\text{SO}_2/\text{Nm}^3$  gas

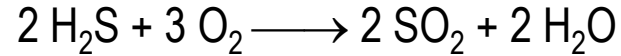


a) The concentration of H<sub>2</sub>S in the gas.

Basis of calculation: 1 m<sup>3</sup> gas

$$\text{H}_2\text{S in 1 m}^3 \text{ of gas} = \frac{3 \text{ g S}}{100 \text{ g gas}} \cdot \frac{1 \text{ mol S}}{32 \text{ g S}} \cdot \frac{1 \text{ mol H}_2\text{S}}{1 \text{ mol S}} \cdot \frac{0.9 \text{ g gas}}{1 \text{ L gas}} \cdot \frac{10^3 \text{ L}}{1 \text{ m}^3} = 0.8438 \text{ mol H}_2\text{S/m}^3 \text{ gas}$$

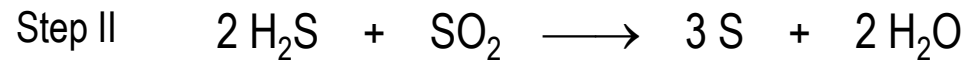
Step I: H<sub>2</sub>S that reacts with 0.05 m<sup>3</sup> air



$$\frac{0,05 \text{ m}^3 \text{ air}}{\text{m}^3 \text{ gas}} \cdot \frac{21 \text{ m}^3 \text{ O}_2}{100 \text{ m}^3 \text{ air}} \cdot \frac{1 \text{ mol O}_2}{22.4 \cdot 10^{-3} \text{ m}^3 \text{ O}_2} \cdot \frac{2 \text{ mol H}_2\text{S}}{3 \text{ mol O}_2} \cdot 0.91 = 0.2844 \text{ mol H}_2\text{S/m}^3 \text{ gas}$$

Production: 0.2844 mol SO<sub>2</sub>/m<sup>3</sup>

Remains: 0.5594 mol H<sub>2</sub>S/m<sup>3</sup>



Limiting reactant

b) The amount of elemental sulfur that can be obtained per m<sup>3</sup> of treated gas.

$$\frac{0,8391 \text{ mol S}}{\text{m}^3} \cdot \frac{32 \text{ g S}}{1 \text{ mol S}} = 26.85 \text{ g S/m}^3$$

c) The amount of residual H<sub>2</sub>S or SO<sub>2</sub> remaining at the end of the process, expressed in mg/m<sup>3</sup> of gas.

$$\frac{4.6875 \cdot 10^{-3} \text{ mol SO}_2}{\text{m}^3} \cdot \frac{64 \cdot 10^3 \text{ mg SO}_2}{1 \text{ mol SO}_2} = 300 \text{ mg SO}_2/\text{m}^3$$

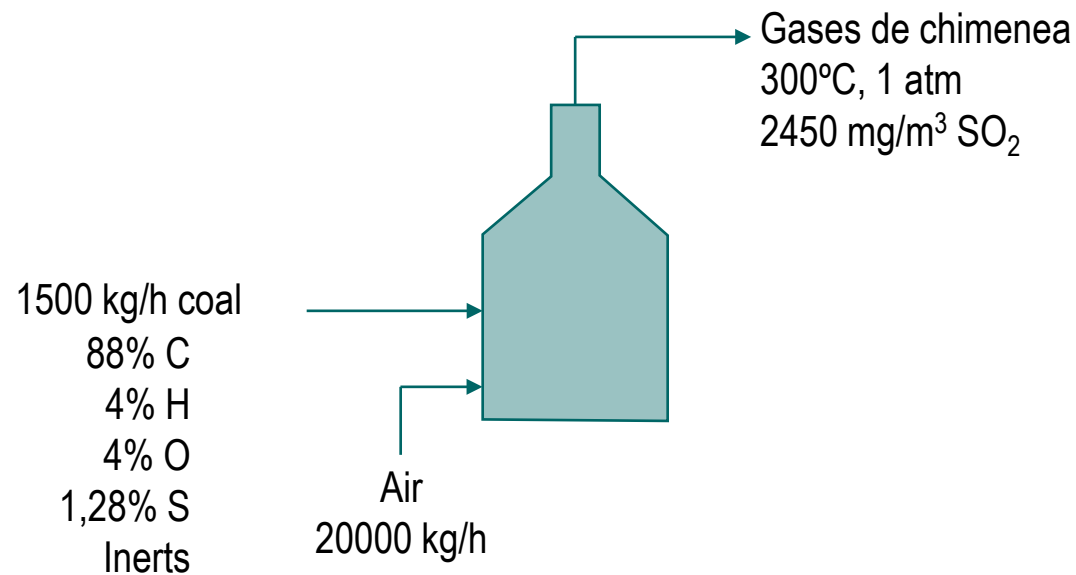
4. 1500 kg/h of coal (88 % C, 4 % H, 4 % O, 1.28 % S, the rest are inert ashes) are burned with air. The air flow used is 20000 kg/h and the flue gas at 1 atm and 300 °C contain SO<sub>2</sub> at a concentration of 2450 mg/Nm<sup>3</sup>. Determine:

a) The flow rate of the flue gas expressed in m<sup>3</sup>/h

b) The excess of oxygen used in percentage.

NOTE: Consider complete combustion for coal.

Answer: a) 32887,60 m<sup>3</sup>/h; b) 17,71%



a) The flow rate of the flue gas expressed in m<sup>3</sup>/h

$$\frac{1500 \text{ kg coal}}{\text{h}} \cdot \frac{1.28 \text{ kg S}}{100 \text{ kg coal}} \cdot \frac{1 \text{ mol S}}{32 \cdot 10^{-3} \text{ kg S}} \cdot \frac{1 \text{ mol SO}_2}{1 \text{ mol S}} \cdot \frac{64 \cdot 10^3 \text{ mg SO}_2}{1 \text{ mol SO}_2} = Q \cdot \frac{2450 \text{ mg SO}_2}{\text{m}^3}$$

Normal conditions  
1 atm, 0°C

$$Q = 15673.47 \text{ m}^3/\text{h} \quad (\text{in normal conditions})$$

$$Q = 15673.47 \text{ m}^3/\text{h} \cdot \frac{573.15 \text{ K}}{273.15 \text{ K}} = 32887.60 \text{ m}^3/\text{h} \quad (\text{at } 300^\circ\text{C and } 1 \text{ atm})$$



b) The excess of oxygen used in percentage.

O<sub>2</sub> required for complete combustion

$$\text{C} + \text{O}_2 \longrightarrow \text{CO}_2 \quad \frac{1500 \text{ kg coal}}{\text{h}} \cdot \frac{88 \text{ kg C}}{100 \text{ kg coal}} \cdot \frac{1 \text{ mol C}}{12 \cdot 10^{-3} \text{ kg C}} \cdot \frac{1 \text{ mol O}_2}{1 \text{ mol C}} = 110000 \text{ mol O}_2/\text{h}$$

$$4 \text{ H} + \text{O}_2 \longrightarrow 2 \text{ H}_2\text{O} \quad \frac{1500 \text{ kg coal}}{\text{h}} \cdot \frac{4 \text{ kg H}}{100 \text{ kg coal}} \cdot \frac{1 \text{ mol H}}{10^{-3} \text{ kg H}} \cdot \frac{1 \text{ mol O}_2}{4 \text{ mol H}} = 15000 \text{ mol O}_2/\text{h}$$

$$\text{S} + \text{O}_2 \longrightarrow \text{SO}_2 \quad \frac{1500 \text{ kg coal}}{\text{h}} \cdot \frac{1.28 \text{ kg S}}{100 \text{ kg carbón}} \cdot \frac{1 \text{ mol S}}{32 \cdot 10^{-3} \text{ kg S}} \cdot \frac{1 \text{ mol O}_2}{1 \text{ mol S}} = 600 \text{ mol O}_2/\text{h}$$

$$\frac{1500 \text{ kg coal}}{\text{h}} \cdot \frac{4 \text{ kg O}}{100 \text{ kg coal}} \cdot \frac{1 \text{ mol O}_2}{32 \cdot 10^{-3} \text{ kg O}_2} = 1875 \text{ mol O}_2/\text{h}$$

O<sub>2</sub> required for complete combustion: 110000 + 15000 + 600 – 1875 = 123725 mol O<sub>2</sub>/h

$$\text{Flow of O}_2: \quad \frac{20000 \text{ kg air}}{\text{h}} \cdot \frac{1 \text{ mol air}}{28.84 \cdot 10^{-3} \text{ kg air}} \cdot \frac{21 \text{ mol O}_2}{100 \text{ mol air}} = 145631.068 \text{ mol O}_2/\text{h}$$

Air average molecular weight: 0.21 · 32 g/mol + 0.79 · 28 g/mol = 28.84 g/mol

$$\text{Excess of air} = \text{Excess of O}_2 = \frac{145631.068 - 123725}{123725} \cdot 100 = 17.71\%$$

b) The excess of oxygen used in percentage.

Alternative procedure

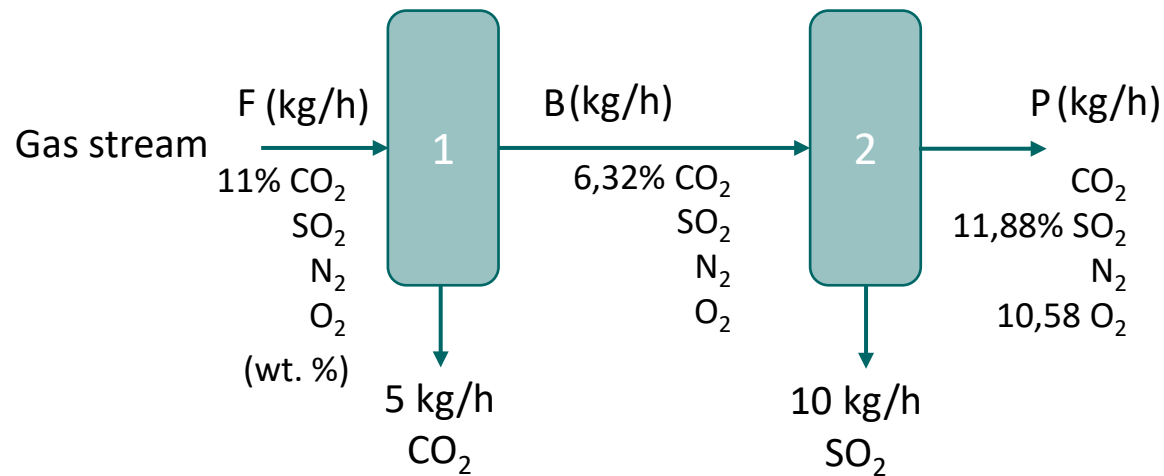
$$\text{Flow of O}_2: \frac{20000 \text{ kg air}}{\text{h}} \cdot \frac{23.15 \text{ kg O}_2}{100 \text{ kg air}} \cdot \frac{1 \text{ mol O}_2}{32 \cdot 10^{-3} \text{ kg O}_2} = 144687.5 \text{ mol O}_2/\text{h}$$

$$\text{Excess of air} = \text{Excess of O}_2 = \frac{144687.5 - 123725}{123725} \cdot 100 = 16.94\%$$

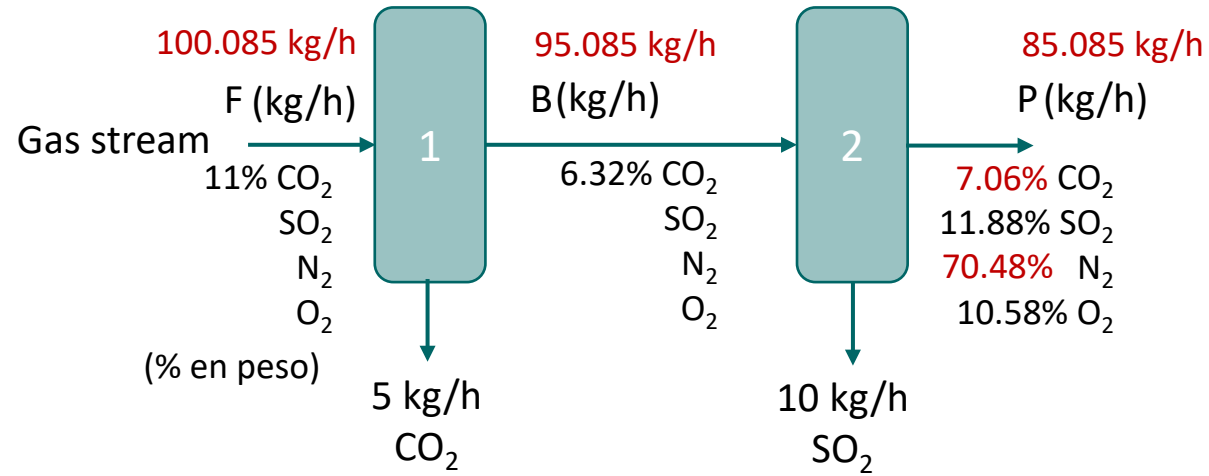
5. A gas stream contains 11% wt. of  $\text{CO}_2$ . Other components of the gas stream are  $\text{SO}_2$ ,  $\text{N}_2$  and  $\text{O}_2$ . This stream is passed through an absorber that only removes the  $\text{CO}_2$  (gas sweetening). After the absorber, the  $\text{CO}_2$  concentration decreases to 6.32% wt. The gaseous stream is then sent to an  $\text{SO}_2$  absorber, the concentrations in the outlet stream from the  $\text{SO}_2$  absorber are 11.88%  $\text{SO}_2$  and 10.58%  $\text{O}_2$ . Considering that 5 kg of  $\text{CO}_2$  and 10 kg of  $\text{SO}_2$  are absorbed per hour:

- Draw a sketch of the process with all the available data.
- Determine the mass flows in the outlet streams of the two absorbers.
- Determine the  $\text{SO}_2$  concentration in the outlet of the first absorber ( $\text{CO}_2$  absorber)
- Determine the composition of the inlet stream to the first absorber

Answer: b) 85.085 kg/h; c) 21.15%; d) 20.09%  $\text{SO}_2$ , 8.99%  $\text{O}_2$ , 59.92%  $\text{N}_2$



a) Draw a sketch of the process with all the available data

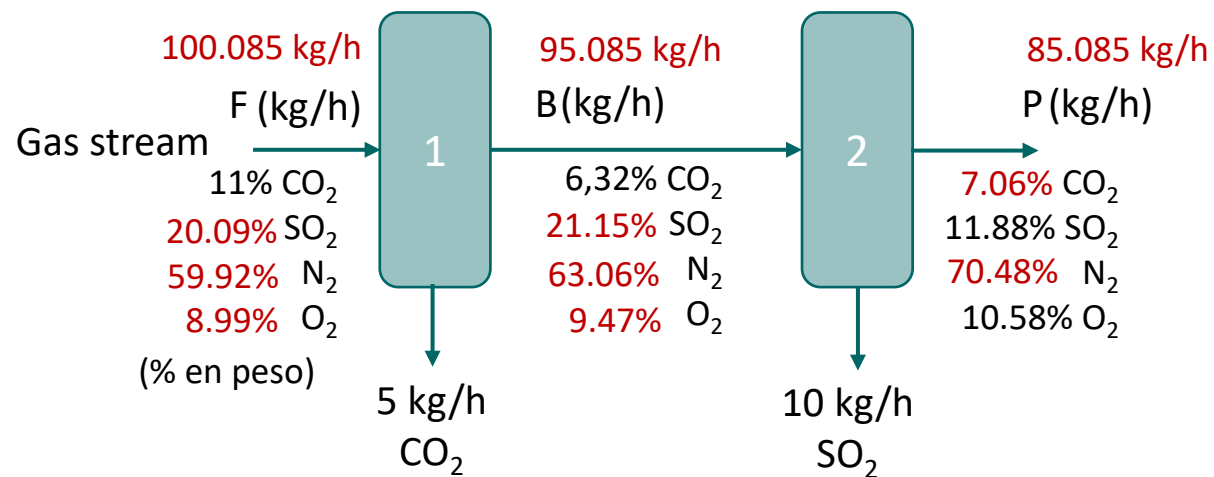


$$\left\{ \begin{array}{l} \text{Global mass balance, absorber 1:} \\ \text{Mass balance to CO}_2, \text{ absorber 1:} \end{array} \right. \Rightarrow \left\{ \begin{array}{l} F = 5 \text{ kg/h} + B \\ 0.11 F = 5 \text{ kg/h} + 0.0632 B \end{array} \right. \Rightarrow \left\{ \begin{array}{l} F = 100.085 \text{ kg/h} \\ B = 95.085 \text{ kg/h} \end{array} \right.$$

$$\text{Global mass balance, absorber 2:} \quad B = 10 \text{ kg/h} + P \Rightarrow P = 85.085 \text{ kg/h}$$

$$\text{Mass balance to CO}_2, \text{ absorber 2:} \quad 0.0632 B = w_{\text{CO}_2, P} P \Rightarrow w_{\text{CO}_2, P} = 0.0706 \Rightarrow 7.06\%$$

$$\text{N}_2 \text{ content in P:} \quad w_{\text{N}_2, P} = 1 - 0.1188 - 0.1058 - 0.0706 = 0.7048 \Rightarrow 70.48\%$$



Mass balance to SO<sub>2</sub>, absorber 2:  $w_{\text{SO}_2, \text{B}} B = 10 \text{ kg/h} + 0.1188 P \Rightarrow w_{\text{SO}_2, \text{P}} = 0.2115 \Rightarrow 21.15\%$

Mass balance to O<sub>2</sub>, absorber 2:  $w_{\text{O}_2, \text{B}} B = 0.1058 P \Rightarrow w_{\text{O}_2, \text{B}} = 0.0947 \Rightarrow 9.47\%$

N<sub>2</sub> content in B:  $w_{\text{N}_2, \text{B}} = 1 - 0.0632 - 0.2115 - 0.0947 = 0.6306 \Rightarrow 63.06\%$

Mass balance to SO<sub>2</sub>, absorber 1:  $w_{\text{SO}_2, \text{F}} F = 0.2115 B \Rightarrow w_{\text{SO}_2, \text{F}} = 0.2009 \Rightarrow 20.09\%$

Mass balance to O<sub>2</sub>, absorber 1:  $w_{\text{O}_2, \text{B}} F = 0.0947 B \Rightarrow w_{\text{O}_2, \text{B}} = 0.0899 \Rightarrow 8.99\%$

N<sub>2</sub> content in F:  $w_{\text{N}_2, \text{F}} = 1 - 0.1100 - 0.2009 - 0.0899 = 0.5992 \Rightarrow 59.92\%$

6. An industry burns 100 t per day of coal with 4% sulfur. It generates 5500 Nm<sup>3</sup>/h of "flue gas" that contains SO<sub>2</sub>, NO<sub>x</sub> and other gases. The NO<sub>x</sub> emission factor is 1.8 kg NO<sub>x</sub>/t of carbon. The NO<sub>x</sub> contains 85% of nitrogen monoxide (NO) and 15% to nitrogen dioxide (NO<sub>2</sub>).

- Determine the concentration of SO<sub>2</sub> in the "flue gas" before the purification process (in mg/Nm<sup>3</sup>).
- Determine the concentration of NO and NO<sub>2</sub> in the "flue gas" before the purification process (in mg/Nm<sup>3</sup>).
- The flue gas is treated and purified with a dry process using calcium carbonate, removing 97% of the SO<sub>2</sub>. Determine the mass (in t) of limestone (90% wt. content in calcium carbonate) consumed per day.

- Determine the concentration of SO<sub>2</sub> in the "flue gas" before the purification process (in mg/Nm<sup>3</sup>).

$$\frac{100 \text{ t coal}}{\text{day}} \cdot \frac{10^6 \text{ g}}{1 \text{ t}} \cdot \frac{4 \text{ g S}}{100 \text{ g C}} \cdot \frac{1 \text{ mol S}}{32 \text{ g S}} \cdot \frac{1 \text{ mol SO}_2}{1 \text{ mol S}} \cdot \frac{64 \text{ g SO}_2}{1 \text{ mol SO}_2} \cdot \frac{10^3 \text{ mg}}{1 \text{ g}} \cdot \frac{1 \text{ h}}{5500 \text{ m}^3 \text{ gas}} \cdot \frac{1 \text{ day}}{24 \text{ h}} = 60606 \text{ mg SO}_2/\text{m}^3$$

b) Determine the concentration of NO and NO<sub>2</sub> in the "flue gas" before the purification process (in mg/Nm<sup>3</sup>).

$$\frac{1,8 \text{ kg NO}_x}{\text{t coal}} \cdot \frac{100 \text{ t coal}}{\text{day}} \cdot \frac{1 \text{ h}}{5500 \text{ m}^3 \text{ gas}} \cdot \frac{1 \text{ day}}{24 \text{ h}} \cdot \frac{10^6 \text{ mg}}{1 \text{ kg}} = 136364 \text{ mg NO}_x/\text{m}^3$$

$$\text{NO}_x \left\{ \begin{array}{ll} 85\% \text{ NO} & 0.85 \cdot 136364 \text{ mg NO}_x/\text{m}^3 = 1159.09 \text{ mg NO}_x/\text{m}^3 \\ 15\% \text{ NO}_2 & 0.15 \cdot 136364 \text{ mg NO}_x/\text{m}^3 = 204.55 \text{ mg NO}_x/\text{m}^3 \end{array} \right.$$

c) The flue gas is treated and purified with a dry process using calcium carbonate, removing 97% of the SO<sub>2</sub>. Determine the mass (in t) of limestone (90% wt. content in calcium carbonate) consumed per day.

$$\begin{aligned} \frac{100 \text{ t coal}}{\text{day}} \cdot \frac{10^6 \text{ g}}{1 \text{ t}} \cdot \frac{4 \text{ g S}}{100 \text{ g coal}} \cdot \frac{1 \text{ mol S}}{32 \text{ g S}} \cdot \frac{1 \text{ mol SO}_2}{1 \text{ mol S}} \cdot 0.97 \cdot \frac{1 \text{ mol CaCO}_3}{1 \text{ mol SO}_2} \cdot \frac{100 \text{ g CaCO}_3}{1 \text{ mol CaCO}_3} \cdot \frac{100 \text{ g limestone}}{90 \text{ g CaCO}_3} \cdot \frac{1 \text{ t}}{10^6 \text{ g}} = \\ = 13.47 \text{ t limestone/day} \end{aligned}$$