INTRODUCTORY COURSE ON HYDROGEN SAFETY AT CENEH - UNICAMP

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ABSTRACT

The course is an introduction to the procedures for safe handling of hydrogen, flammable and toxic gases by small users working in the field of hydrogen and fuel cells. Theoretical and practical aspects are emphasized, aiming at identifying the main hazards and reduce the risks associated with the use of these gases. Topics: 1. Market, hydrogen production, fuel cells, and energy storage; 2. International System of Units, Comparison between the ideal gas and real gases; 3. Safety of gases and hydrogen; 4. Cylinders, fittings and valves for gases and hydrogen; 5. Purge of gases; 6. Infrastructure for gases and hydrogen; 7. Accidents with hydrogen.

1. INTRODUCTION

The course was based on the experience accumulated by Hydrogen Laboratory at Universidade Estadual de Campinas (LH2-UNICAMP), since its foundation in 1975, including technologies such as production, purification, storage, analysis and utilization of hydrogen. During 18 years, the laboratory operated a plant producing hydrogen from alkaline water electrolysis and cryogenic purification. The gas was compressed in diaphragm compressors up to 18 MPa, and stored in cylinders with hydraulic volume of 42 to 50 L. This plant produced 90 kg of hydrogen per month for several years, and the gas was used in the research at the laboratory, in other laboratories at Unicamp, by CPqD - Telebras and gas companies. Trace gas analysis of gas samples taken from all cylinders indicated a high purity gas, 99.9995 %mol/mol. The few contaminants were nitrogen, oxygen (gas chromatography) and water (dew point meter), less than 2 μmol/mol each, and 5 μmol/mol or less in total. To achieve these results, it was necessary to develop equipment (electrolyzers and purification plants) and methodologies for gas purification, cylinder cleaning, gas sampling, gas analysis, trace gas standards, and also plant safety. In the 80s and 90s the laboratory performed experiments with hydrogen in Otto cycle and diesel internal combustion vehicles, and developed an experimental fuel cell vehicle, increasing the interest in safety for vehicular applications. In 2002 the cycle of conferences International Workshop on Hydrogen and Fuel Cells - WICaC began, and since then the Hydrogen Safety Course is being offered as a parallel activity for the attendees. The same year saw the launch of the Program of Science, Technology and Innovation for Hydrogen Economy - ProH2, of the Ministry of Science, Technology and Innovation. One topic of greatest interest was reformers of ethanol and natural gas, of medium capacity, aiming at distributed generation of hydrogen. Given the increased scale of projects by teams that were more used to the development of catalysts using micro-reactors, it was considered appropriate to extend the course objectives to include topics on toxic and asphyxiating gases. This paper presents the main subjects and concepts that constitute the Introductory Course on Hydrogen Safety at CENEH-UNICAMP that has served approximately 150 students.

2. OBJECTIVES OF THE INTRODUCTORY COURSE ON HYDROGEN SAFETY

The course objectives are: i) To provide essential tools for small users, so they can make safe use of hydrogen in research, development or processes. ii) To extend the concepts to include flammable, toxic and simple asphyxiating gases that are also widely used in R&D and industrial activities. iii) To make the students able to identify weaknesses in the infrastructure, systems and procedures that they are using in order to correct them. iv) To motivate the students to think about safety procedures to protect themselves and their teammates. v) To raise the level of responsibility of the participants through examples, videos, photos and case studies.

3. ABOUT THE COURSE

The course is taught in classroom using presentations and videos, and is divided into modules of 90 min, 6 h/day, 12 h in total. The basic course addresses the following topics: 1) National and International Markets, Hydrogen Production, Fuel Cells and Energy Storage; 2) International System of Units; Comparison of Ideal Gas and Real Gases; 3) Safety of Gases and Hydrogen; 4) Cylinders, Fittings and Valves for Gases and Hydrogen; 5) Gas Purges; 6) Infrastructure for Gases and Hydrogen; 7) Accidents with Hydrogen. The course can be extended for up to 30 h, if the students have interest in assembling gas systems, leak detection, trace gas analysis of pure hydrogen, or how to operate equipments with hydrogen.

4. H_2 MARKET AND PRODUCTION, FUEL CELLS, ENERGY STORAGE

This topic addresses the main industrial uses of hydrogen, the domestic and international markets, production methods (alkaline water electrolysis and fuel reforming), a comparison of energy storage in batteries and hydrogen.

5. INTERNATIONAL SYSTEM OF UNITS, COMPARISON BETWEEN IDEAL GAS AND REAL GASES

5.1. International System of Units

Good communication of measurements and parameters of process is essential to ensure the safety of personnel and facilities, both in laboratory and industry. This topic reviews the International System of Units (SI), the rules to properly express quantities and their units, with special attention to the units of temperature, pressure and concentration, which are essential when working with gases [1, 2].

In Brazil, the SI is adopted since 1962, and its use is mandatory. It is recommended that students consult the website of the National Institute of Metrology - INMETRO, Brazil [1] and the Bureau International des Poids et Mesures - BIPM [3]. In other countries there are institutes that maintain instructional content on the topic in their websites, such as NIST site [4].

A key recommendation of this topic is that derived units should be written using the same rules used for mathematical expressions, for example: use $kg.m^{-1}.s^{-2} = kg/(m.s^2)$ and not $kg/m/s^2$ (wrong).

The following units of pressure are not recommended: atm, psi, psig, psia, kgf/cm^2, torr. They should be replaced by SI units of pressure, as hPa ou kPa for atmospheric pressure, and MPa, for high pressures.

The following units of pressure are not recommended: ppm, ppmv, ppv, PPB, ppt. They do not provide adequate information about the calculation basis (mass, volume, quantity of matter) and can lead to important errors of interpretation, compromising safety. Concentrations can be expressed in a concise and elegant way by SI units, such as: mol/m^3, kg/m^3, g/L, mg/L, mg/m^3, %L/L, %mol/mol. The unit used for amount of substance is “mole”, and its concept must be well understood by the students, because it is the most important unit to express concentrations of gases [5].

Table 1 presents the units and common SI prefixes used to express concentration of gases. In general, the calculations are facilitated with those units. A useful format to work in extensive concentration ranges, from traces to percentage values, is 0.0000% mol / mol, where the last decimal figure represents μmol/mol.

Table 1. SI Units and prefixes used to express concentrations of gases.

Not recommended		Value	Recommended	
Name	**Symbol**		**Symbol**	**Name**
percent	%, %v/v	10^{-2}	%mol/mol	percent mol per mol
parts per million	ppm, ppmv, ppv	10^{-6}	μmol/mol	micromol per mol
parts per billion	Ppb	10^{-9}	ηmol/mol	nanomol per mol
parts per trillion	Ppt	10^{-12}	pmol/mol	picomol per mol

Although Nm^3 and Nl, normal cubic meter and normal liter, appear regularly in literature as standard units to express gas volume, their use should be discontinued due to strong arguments. First, in SI the symbol N is reserved for the unit of force, newton. Originally Normal Temperature and Pressure (NTP) refer to 273.15 K and 101 325 Pa. But today IUPAC adopts 273.15 K and 100 kPa as the “standard conditions for gases” [6], and there are many institutions defining “normal” or “standard” conditions differently. To overcome this difficulty, we recommend to use m^3 (or L) and inform in the text, just once, that the volumes were measured at 273.15 K and 100 kPa, otherwise one should inform the actual conditions. Additionally, a good practice to avoid problems with quantification of gases is to use units of mass units (g, kg, t) instead of units of volume.

5.2. Comparison between Ideal Gas and Real Gases

In this topic, the ideal gas equation, $p\,V = n\,R\,T$, is reviewed and its practical application is discussed. The students are reminded that in this equation one should use absolute pressure, Pa, and thermodynamic temperature, expressed in kelvin, K. The absolute pressure, symbol p_{abs}, is zero-referenced against a perfect vacuum, so it is equal to gauge (or manometric) pressure, symbol p_{man}, plus atmospheric pressure, symbol p_{atm}, synthesized by Equation 1:

$$\boldsymbol{p_{abs} = p_{man} + p_{atm}} \quad , \tag{1}$$

Another important point to emphasize in terms of safety is that reservoirs at 0 bar gauge pressure are filled with gas at atmospheric pressure, which should be taken into account in activities with toxic or reactive gases, such as carbon monoxide or oxygen and hydrogen, respectively. In such cases, the gas inside the reservoir must be properly discarded or neutralized.

Other equations of interest for calculations with real gases are also presented and discussed, using compressibility factors, densities and concentrations, as well as Figure 1 and Table 2 that show the differences between molar densities (mol/L) of the ideal gas and real gases in function of pressure.

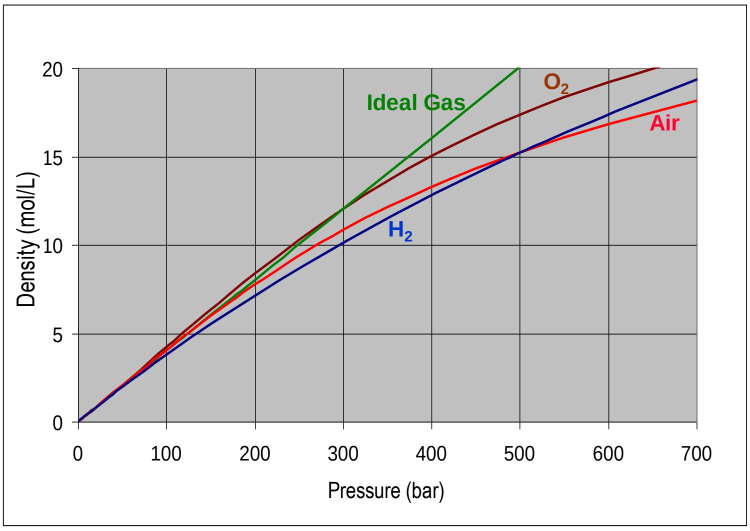


Figure 1: Density (mol/L) in function of pressure for the Ideal Gas and Real Gases.

Table 2. Deviation from the ideal behavior of gas densities (mol/L): *Desvio* = D_{real} / D_{ideal} - 1

Gas	10 bar	50 bar	100 bar	200 bar	700 bar
Helium	-7.6%	-8.3%	-11.0%	-14.0%	*
Hydrogen	-0.6%	-2.9%	-6.0%	-11.0%	-31.0%
Nitrogen	0.2%	0.3%	-0.5%	-5.0%	-38.0%
Air	0.3%	1.0%	0.0%	-3.0%	-35.0%
Oxygen	0.6%	2.8%	5.0%	5.0%	-26.0%

T = 27 °C = 300 K

6. ACCIDENT PREVENTION, SAFETY OF GASES AND HYDROGEN

This module covers the following topics: i) General considerations about accidents; ii) Accidents with gases; iii) Conditions for combustion and detonation; iv) Characteristics of hydrogen and comparison with other gases; v) Safety procedures; vi) Hazards Form; vii) Confined spaces.

6.1. General considerations about accidents

There are several versions of the pyramid of accidents on the web, but in general they refer to the book of H.W. Heinrich, Industrial Accident Prevention: a scientific approach, and citations about the DuPont company that relates one fatal accident for every 30,000 unsafe acts or conditions. Our view on the matter is that in the daily activities of companies and industries accidents can be avoided in most cases. For a major accident to occur, a chain of events or actions is needed, which can also mean that there are many opportunities to avoid it. Anyway, the responsibility of an accident prevention or accident occurrence falls on the whole team.

Figure 2 presents our own version of the pyramid of accidents, indicating that the types of accidents and their frequency keep a close relationship. In the figure, n = 1, 2, 3, ... is a number that may depend on the type of activity and the specific conditions of each unit (industry, lab, etc..), such as commitment with safety management, staff training, investments made in safety, etc.

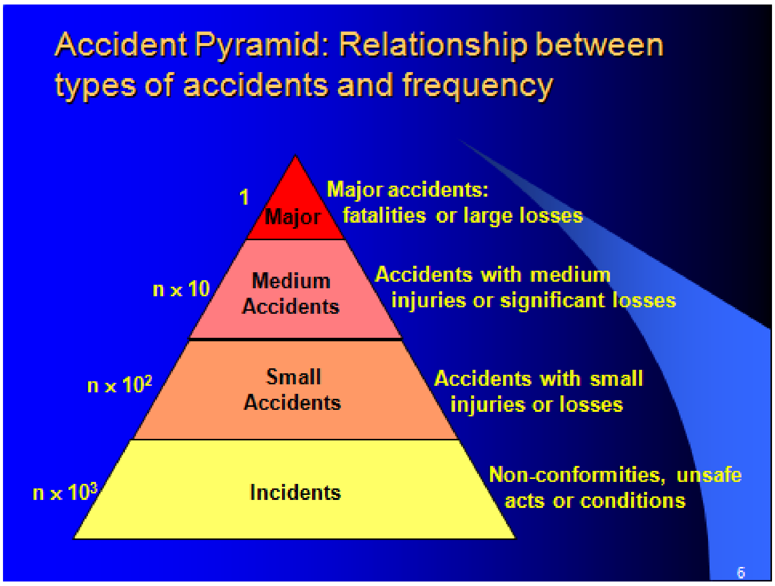


Figure 2: Accident Pyramid relates the severity of accidents with their frequencies.
Additional details on the text.

6.2. Accidents with gases

Working with gases is no different, accidents can be avoided. And it is surprising how a few basic rules can make working with gases much safer. According to the UN, the gases can be classified as flammable, non-flammable and non-toxic, and toxic gases. But in many cases, the gases have characteristics of more than one group.

According to surveys conducted for the course, the following general observations can be made on gases: i) All gases are suffocating, with the exception of atmospheric air. (Note: the excess oxygen can also cause health problems and tremendously accelerate combustion.) ii) The risk of choking occurs when atmospheric air is displaced or diluted by other gas, making the oxygen available insufficient to maintain life. iii) Some gases are odorless and colorless and their presence cannot be perceived by people. v) When the symptoms appear it may already be too late. v) Important: people may have very different tolerances for gases.

Figure 3 presents some possible consequences for the leak of asphyxiating, poisonous and flammable gases. The main message of the course in this topic is that in all cases the worst consequence is death or permanent disability, no matter what type of gas leaks. Therefore, safety measures should always be followed strictly when working with gases.

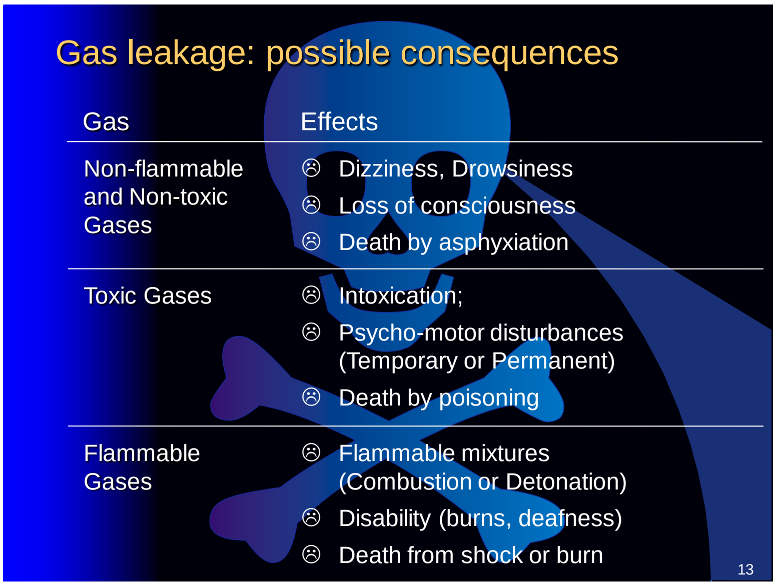


Figure 3: Gas leaks and possible consequences.

Preventive measures against asphyxiation are: 1) Avoid handling gases indoors; 2) Properly ventilate the environment; 3) Any discharge of gases must be directed out of the room; 4) Do not work alone; 5) "Open cylinder" means "cylinder in use"; 6) Periodically check for leaks.

Toxic gases represent a greater risk because the inhalation of small amounts at low concentrations (trace levels) may compromise the health or lead to death. A classic example is the poisoning and death of people in closed garages caused by carbon monoxide present in the exhaust gas of automobiles. This gas attaches to the hemoglobin of blood and greatly reduces cellular respiration [2]. Preventive measures against toxic gases include: i) To know the characteristics of the products, necessary care for their manipulation, symptoms in case of exposition, and first aid. ii) The manipulation must be done in sealed rooms or cabinets, both with exhaustion. iii) Additional measures: use of gas sensors, washing the exhaust gases to sequestrate toxic gases, negative pressure in the room, etc. iv) Properly ventilate the working environment. v) Do not work alone. vi) Use of appropriate PPE (personal protective equipment) to attend an emergency: mask with valve, portable air cylinder, etc.

The NIOSH Pocket Guide to Chemical Hazards is an important source of information about chemical substances and their hazards. Figure 4 shows the NIOSH's page for carbon monoxide [7], as an example. Some of the main parameters, such as IDHL, REL and TWA, are presented and discussed. Brazilian students are also informed that the site of Cetesb - SP (Environmental Company of the State of São Paulo) offers important information about Chemical Emergencies [8] and has a manual and a course on risk analysis [9].

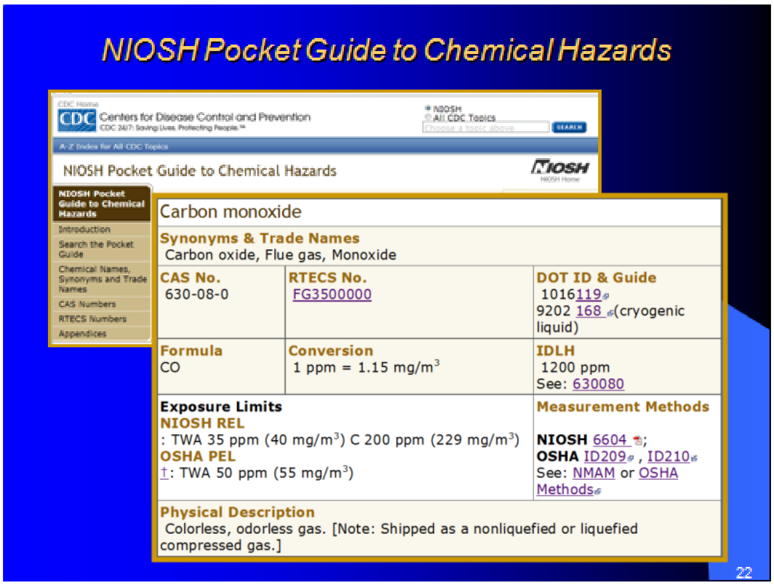


Figure 4: Carbon monoxide information sheet in the NIOSH Pocket Guide.

The following techniques for leak detection are discussed: i) Aqueous solution of ethanol at 50 %L/L (major leaks); ii) aqueous solution of 25% to 50 %L/L liquid detergent (small leaks); iii) Pressure drop: $p_i/T_i = p_f/T_f$; iv) Leak detector (conductivity detector or mass spectrometer); v) Sensors for organic vapors and fuel (photo-ionization).

Preventive measures against flammable gases are similar to measures adopted to asphyxiating and poisonous gases. In fact, dilutions by purging or ventilation are among the main measures to prevent the fuel - air mixture to reach the range of detonation.

6.3. Conditions for combustion and detonation

In this section the conditions to start and maintain fire (combustion) and to produce detonation are discussed, and the fire tetrahedron is presented to the students. Figure 5 and Figure 6 show graphs of flame speed in function of hydrogen concentration, and the limits of flammability and detonation of mixtures H_2 - Air.

6.4. Physicochemical characteristics of hydrogen compared to other gases

This topic presents the physicochemical characteristics of hydrogen, the energy density compared to other fuels, materials compatibility, hydrogen embrittlement, etc. It is a good opportunity to discuss some myths, such as that hydrogen is dangerous because it is flammable. The instructor remembers that all fuels are flammable, and therefore they are used as such. Other very favorable characteristics that should be mentioned are that the energy content of hydrogen per volume is significantly smaller than that of natural gas and it will disperse more easily than the other gases.

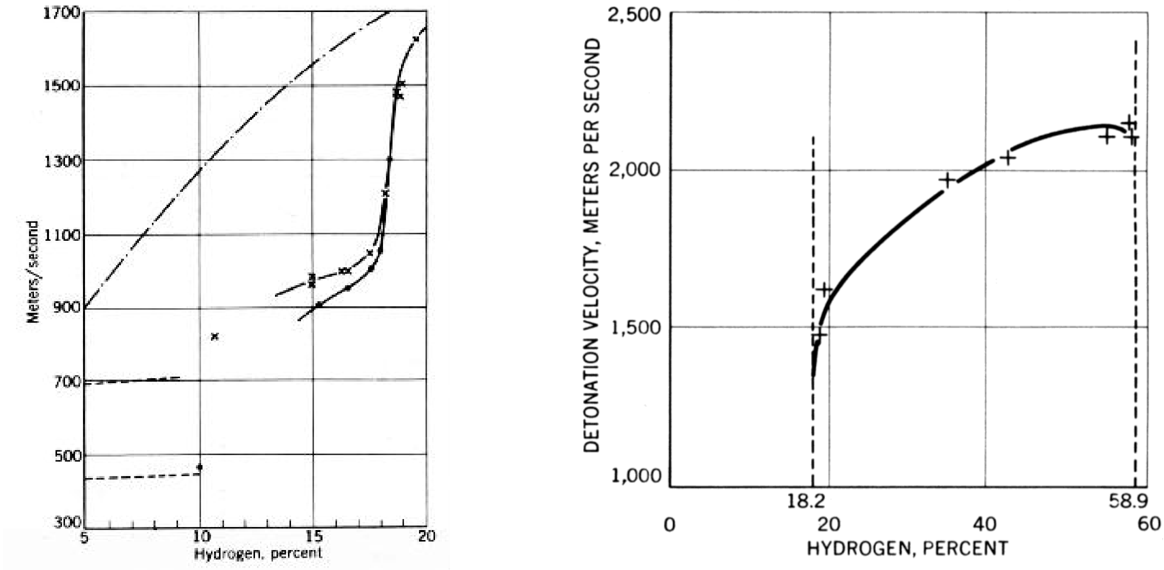


Figure 5: Detonation speeds are significantly higher than combustion speeds for H_2 - Air mixtures [10]. One can observe a significant increase in the flame speed for H_2 concentrations varying from 15 %mol/mol to 20 %mol/mol, and every effort must be made to prevent this condition is reached.

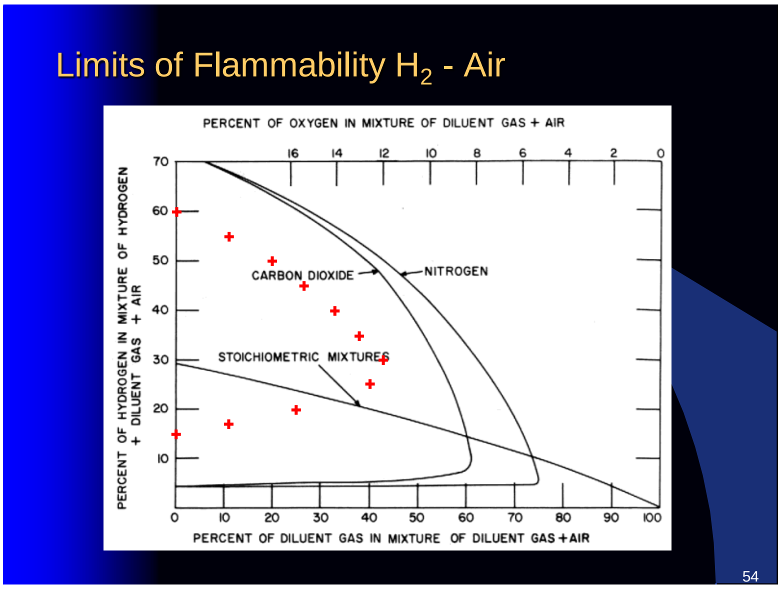


Figure 6: Limits of Flammability of mixtures H_2 - Air in presence of a diluent gas (nitrogen and carbon dioxide) [10]. The red crosses represent the Limits of Detonation estimated by the author; and the region inside the crosses must be avoided in order to prevent detonation.

6.5. Safety procedures

A very important goal of the course is to motivate students to think on safety procedures continuously. Many laboratories do not have teams dedicated to safety and do not have a culture focused on safety. For this reason it is very important to encourage everyone to take part in the discussions about the procedures, best practices and standards to be adopted, making them co-responsible for safety in their work environment. R&D activities in laboratories usually are quite diverse, which also hinders the establishment of safety measures by external members of the group. Thus, the following points are addressed to the students: i) Safety procedures should be established for the entire team. ii) Simple is better! iii) The group should reach a set of rules that can be followed by all, otherwise they will be circumvented. iv) To work safely, some extra work is inevitable, and everyone have to be aware of this. iv) Only the person in charge (leader or manager) can approve and modify safety procedures. v) Any member of the team has the right to warn and stop the activity in course in case of violation of the established rules. vi) It is very important to have those rules set in advance. vii) Each person is responsible for its own safety in order to keep its teammate safe.

6.6. Hazards Form

The form shown in Table 3 is based in a model developed by Companhia Energética de Minas Gerais - Cemig, which sent two teams to have training on hydrogen safety at the LH2-Unicamp few years ago. The form assists in the experiment planning, helping to identify hazards and to select measures to mitigate the risks. The advantages and difficulties to create a support team with defined functions, such as driver, guardian angel, operator, etc. is discussed. But undoubtedly, this support will enable a much faster and effective response in case of accidents.

Table 3. Hazards and risk mitigation form

Hazards Form	**LH2 / IFGW / UNICAMP**	File #:	Date:	Hour:

Project			
Task			
Objectives			
Responsible			
Participants			
Support	Guardian Angel:	Driver:	Operator:
Emergency	Hospital/First Aid:	Fire Brigade:	Safety Cmte:

Dangers / Accidents		
1. ☐ High Pressure	9. ☐ Animals / Insects	18. ☐ Falling Object
2. ☐ Explosion	10. ☐ Excessive Heat / Cold	19. ☐ People Falling
3. ☐ Fire	11. ☐ Physical / Mental Fatigue	20. ☐ Radiation
4. ☐ Projectiles / Sparks	12. ☐ Electrical Shock	21. ☐ Voltage Return
5. ☐ Chemical Products	13. ☐ Injury / Wound	22. ☐ Excessive Noise
6. ☐ Asphyxia	14. ☐ Communication Failure	23. ☐ Excessive Humidity
7. ☐ Flammable Gases	15. ☐ Improper Illumination	24. ☐ Vibration
8. ☐ Toxic Gases	16. ☐ Environmental Impact	25. ☐ Other
	17. ☐ Crane Operation	26. ☐ Other

Description of activities	Dangers	Measures for risk mitigation
1.		
2.		

6.7. Confined Space

In search of information for improving the topic on accident prevention with gases, we found interesting Brazilian regulation and codes about confined spaces [11, 12, 13], and plenty of international information on the subject, for example, in the OSHA website [14]. Confined spaces are enclosed or partially enclosed areas where the atmosphere changes continuously, either by the entrance or evolution of gases, either because the oxygen content decreases. They should not be continuously occupied by workers, their access must be controlled, and the oxygen content must be monitored to range between 19.5 %mol/mol% and 23.0 %mol/mol. Lower concentrations can lead to suffocation, while higher concentrations may lead to accelerated burning.

Some buildings, rooms and laboratories may require the same care as confined spaces. People have to think seriously about it, because apparently safe environments can become death traps even with the emergence of small gas leaks. A video is shown at the end of this module, reporting the accident at the refinery Valero Energy Corp., Delaware, USA, in 2005, where two workers died from asphyxiation when entering a reactor containing nitrogen, a gas considered harmless by the inexperienced. According to reports, the results of suffocation is immediate and the victim falls on his knees and then to the ground without any possibility of reaction. To test the effect of choking, students are asked to hold their breath with lungs full of air. Then, they empty their lungs and repeat the test. The apnea time in the second case is significantly shorter, giving a good idea of what will happen in the case of inhalation of a gas with low oxygen content.

7. CYLINDERS, CONECTIONS AND VALVES FOR HYDROGEN AND COMPRESSED GASES

This topic discusses practical aspects of the subjects listed in the title. With respect to cylinders, the following recommendations inform what should never be done: i) ... repair a cylinder or its valve, or modify features or color. ii) ... move a cylinder without a metal cap. iii) …remove a butterfly cap from a cylinder. iii) ... connect a cylinder that is not attached to a wall or appropriate support. iv) ... leave a cylinder open when it is not in use. v) ... lift a cylinder with a cable, electromagnet or crane. vi) ... displace a cylinder by rolling it in a horizontal position. viii) ... try to catch a falling cylinder.

With the help of Figure 7 and short videos, students are instructed on how to perform small displacements of cylinders. Basic information on how to deal with emergencies related to hydrogen is also presented.

Figure 7: Recommendations about cylinder displacement, horizontally (left) and vertically (right).

Figure 8, Left: shows some connections for inert, flammable and oxidizing gases. Right: needle valves recommended for working with gases must have polymer seals, which are able to tolerate dust and minor irregularities. Students are also faced with the fact that all valves leak. When they are new and properly closed, they leak slightly, otherwise significant leaks may occur. This requires a good planning of gas systems, appropriate maintenance and safety measures to prevent the formation of explosive gas mixtures in reactors, sealed reservoirs, piping, etc.

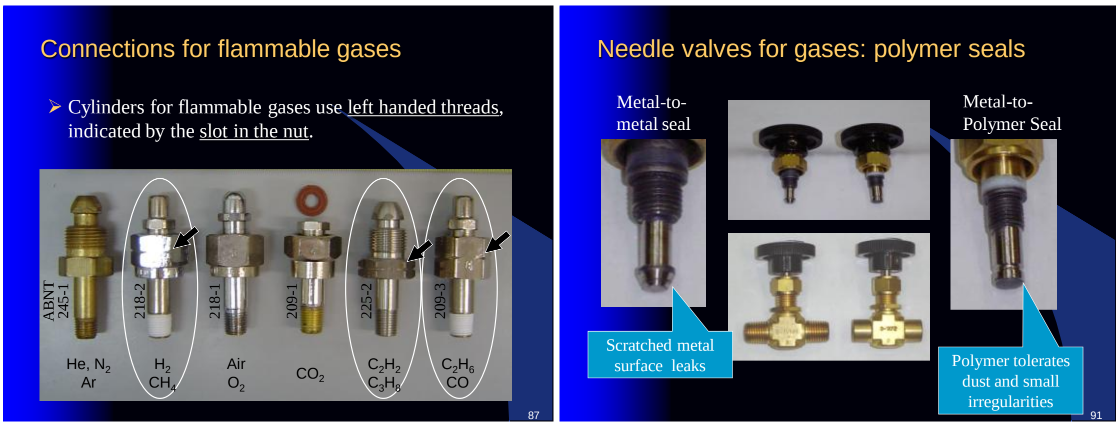


Figure 8, Left: connections for inert, flammable and oxidizing gases. Right: needle valves with polymer-metal sealing are recommended for gases to minimize the leaks.

To complete this module, practical information is presented about metal connections, fittings, double ferrules for copper and stainless steel tubes, pressure regulator valves with small internal volume for pure gases and analytical purposes, plastic pipes and fittings, and maximum working pressure allowed in systems with many components.

8. PURGES OF GASES

When working with gases, to purge means to wash a tank, pipeline or system with gas, or relieve the pressure of a system. Purges can be made for preparative purposes, for cleaning the system to receive a pure gas or a different gas; analytical purposes, to obtain a representative sample of a gas to be analyzed; and safety purposes, to neutralize a flammable gas, to put it out of the flammable range. Different types of purge are discussed, didactically classified as: i) gas blow purge, ii) purge by continuous dilution iii) step by step purge. At the end of this module, some additional comments are made about gas sampling for trace gas analysis.

Step by step purge typically occurs in pipes, where the length is much greater than the diameter, which facilitates the displacement of the gas by simply blowing the pipe with another gas at slightly higher pressure.

Purge by continuous dilution occur in reservoirs where the diameter is larger than the diameter of the gas pipe, which causes preferential flow routes and the emergence of "dead volumes", which are regions more difficult to be reached by the purge gas. The same principle applies to the ventilation of environments, such as rooms. Equation 2 allows estimating the behavior of continuous purges in environments with natural or forced ventilation or leaks in a room. This equation was developed based on NFPA 69 ed. 2008, Annex D [15]. It is quite versatile, and can also be used to calculate gas purges in reservoirs.

$$\boldsymbol{C} = \boldsymbol{C_0} \times \mathbf{exp}\left(-\boldsymbol{K} \times \frac{\boldsymbol{V}}{\boldsymbol{V_0}}\right) \quad , \tag{2}$$

where C - concentration, %mol/mol; C_0 - initial concentration of the gas of interest, %mol/mol; K - mixing efficiency factor, dimensionless; V - volume of the purge gas, L; V_0 - volume of the room or reservoir (at p_{atm}), L.

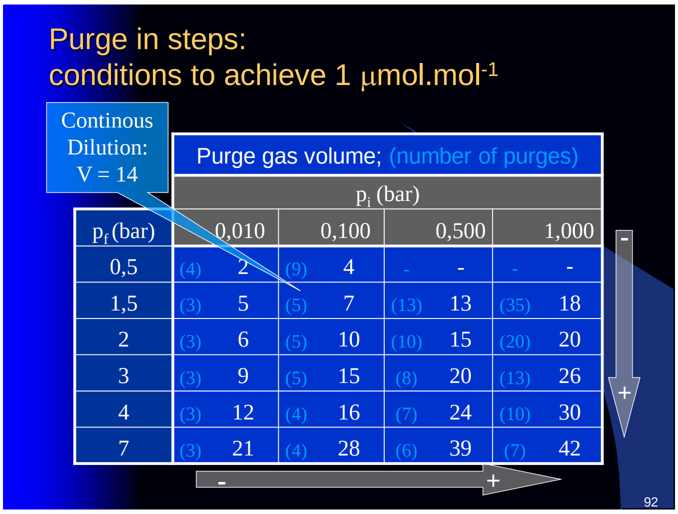
The K factor is measured experimentally and expresses the efficiency with which the gases get mixed. Small values of K mean that more time or more gas will be necessary to complete purge procedure. For example, the K varies from 0.2 for natural ventilation via an open door or window, to 0.9 for forced ventilation of air through multiple vents.

Step by step dilution, represented by Equation 3, is accomplished by lowering the pressure of the reservoir as much as possible (p_i), and elevating the pressure with the purge gas (p_f), repeating this procedure for each step. For practical results it is necessary that $p_f >> p_i$.

$$\boldsymbol{C_k(A)} = \boldsymbol{C_0(A)} \times \left(\boldsymbol{K} \times \frac{\boldsymbol{p_i}}{\boldsymbol{p_f}}\right)^{\boldsymbol{n}}, \ \boldsymbol{k} = \mathbf{0}, \mathbf{1}, \mathbf{2}, \ldots \quad , \tag{3}$$

where $C_k(A)$ - concentration of component A in step k, %mol/mol; $C_0(A)$ - initial concentration of A, %mol/mol; p_i - initial pressure (low) at the beginning of the step, bar; p_f - final pressure (high) at the end of the step, bar; n - number of steps.

The best results are obtained using vacuum, which contributes to a small consumption of purge gas, less incidence of contamination and assuring that all points of a complex system will be reached. Figure 9 shows estimations of the purge gas consumption and the number of steps necessary to purge a reservoir from [A] = 100 %mol/mol to achieve 1 μmol/mol using step by step purge.



p_f (bar)	p_i (bar) 0,010	0,100	0,500	1,000
0,5	(4) 2	(9) 4	- -	- -
1,5	(3) 5	(5) 7	(13) 13	(35) 18
2	(3) 6	(5) 10	(10) 15	(20) 20
3	(3) 9	(5) 15	(8) 20	(13) 26
4	(3) 12	(4) 16	(7) 24	(10) 30
7	(3) 21	(4) 28	(6) 39	(7) 42

Figure 9: Results of step by step purge of a gas inside the reservoir to reach a concentration of 1 μmol/mol, for different pressures (absolute). In the example shown, the volume of purge gas consumed is equal to 7, expressed in number of times the hydraulic capacity of the reservoir. Accomplishing the same task by continuous dilution (K = 1) doubles the volume of purge gas, 14.

This section is completed with information about the necessary procedures to purge reservoirs of variable volume, such as cleaning gas sampling bags and syringes to collect gas samples for analysis, and a gasometer, to diminish the oxygen concentration, allowing the storage of hydrogen and other combustible gases.

9. INFRASTRUCTURE FOR HYDROGEN

This section aims to offer to students some basic concepts on infrastructure for hydrogen and gases. Regulations, Codes and Standards are addressed in an additional module, not contained in this article. One of the most emphasized points refers to the choice of materials to work with hydrogen. Manufacturers or distributors must inform the technical characteristics and, ultimately, it is recommended that the material be tested. Under no circumstances one should use unknown materials or with incomplete information. In general, AISI 316 stainless steel, brass and some aluminum alloys are suitable for working with hydrogen. In the case of AISI 304 stainless steel, it is necessary to take special care with the surface finish, otherwise it may suffer embrittlement. Electrochemical processes for machining or finishing can also introduce hydrogen into the material, making it susceptible to embrittlement. Welds are usually safe, but can change the material characteristics. Therefore, attention is needed in the choice of material, service execution, and annealing may be necessary. If one can summarize in one sentence the care to be taken with the choice of materials for use with hydrogen, it would be: do not take the risk, get informed!

With respect to the handling of hydrogen, the main recommendation is to do that in an open, well ventilated area whenever possible. In buildings one should promote adequate ventilation to dilute or disperse the gas in case of leaks. Confinement must be avoided to the maximum because open clouds of hydrogen hardly detonate, although they can burn and cause injuries.

With regard to electrical equipment for hydrogen, the standard NFPA 70, Class I, Division 2, Group B, provides good guidance. In Brazil, one should use the standard ABNT NBR IEC 60079-14:2009, Explosive atmospheres Part 14: Electrical installations design, selection and erection. Considering that armored and explosion proof equipment is very expensive, the sockets, switches and electrical equipment should be installed at a safe distance from possible sources of leaks. These recommendations will lower the classification of areas, reducing installation costs. Figure 10 presents some suggestions about construction details to work with hydrogen.

Figure 10: Construction details contribute to avoid accumulation of hydrogen and reduce the area classification. Details of passive protection, which acts continuously, are shown. There is also some active protection, which requires electrical devices, maintenance and some management effort.

At the end of this module, different types of sensors for hydrogen, toxic and combustible gases are presented, such as solid state sensors, electrochemical, photoionization, flame ionization and thermal conductivity. Depending on the interest of the group, the main characteristics, applications, advantages and disadvantages of each type of sensor may be discussed.

It is also recommended to Brazilian students to read articles that may assist them in the licensing process of hydrogen projects, such as risk analysis, regulation, codes and standards [16, 17, 18].

10. ACCIDENTS WITH HYDROGEN

In this module some of the accidents involving hydrogen are presented and discussed, highlighting that some of them were caused by other reasons. In all cases, however, detailed investigation of the accident, and the examination of all related documents is very important to enable its explanation. This activity allows the development of technical standards and procedures that will help to prevent other accidents. Students are motivated to deepen their knowledge on the subject and as a starting point two sources with extremely valuable information and high technical content are suggested [19, 20].

The cases selected for presentation in the course are: i) Tempelhof Field, 1884, where about 400 hydrogen cylinders exploded without any apparent reason. The investigation showed that inappropriate material had been used with hydrogen. ii) Hanau Accident, 1991, where a tank with 100 m^3 of hydrogen exploded. Research has shown that hydrogen embrittlement was the cause of the accident, which led to a complete revision of standards for cylinder manufacturing in Germany, the lifetime calculation, detection of cracks and huge progress in safety engineering. iii) Airship Hindenburg in Lakehurst, 1937, which caught fire with 97 passengers on board, causing the death of 35 passengers. Twenty seven of them jumped from the airship in flames and eight were burned by diesel. The accident has been widely documented with movies and photos, being responsible for the high risk perception associated with hydrogen by the public. But it is possible to show that despite the huge amount of hydrogen, 18 t, no detonation occurred, only combustion, allowing the airship to fall from a height of 70 m relatively smoothly. The causes of the accident are discussed as well as the physicochemical properties of hydrogen that helped to limit its consequences: nontoxic, low thermal radiation, and rapid dispersion. iv) Space Shuttle Challenger disaster, in 1986, where a seal failure in the right-side solid rocket booster allowed the hot gas to damage the structure, leading to the destruction of the space shuttle. v) Accident with natural gas vehicle, occurred in Brazil some years ago, caused by unauthorized misuse of a LPG cylinder to increase the autonomy of the vehicle. The photos of this accident are very didactic, showing the disruption of the LPG cylinder in two halves, the complete destruction of the vehicle and, on the other hand, the CNG tank was intact. If correctly explored, cases like this serve to demonstrate the excellent safety achieved by CNG cylinders, and that vehicles using natural gas or hydrogen are safe, provided the safety standards are followed.

11. CONCLUSION

This article describes the subjects and the approach used in the introductory course on hydrogen safety, based on the experience of the LH2-Unicamp in R&D of hydrogen technologies since it was founded in 1975. The course has helped approximately 150 students and the expectation is that this content can be made available online in the near future.

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