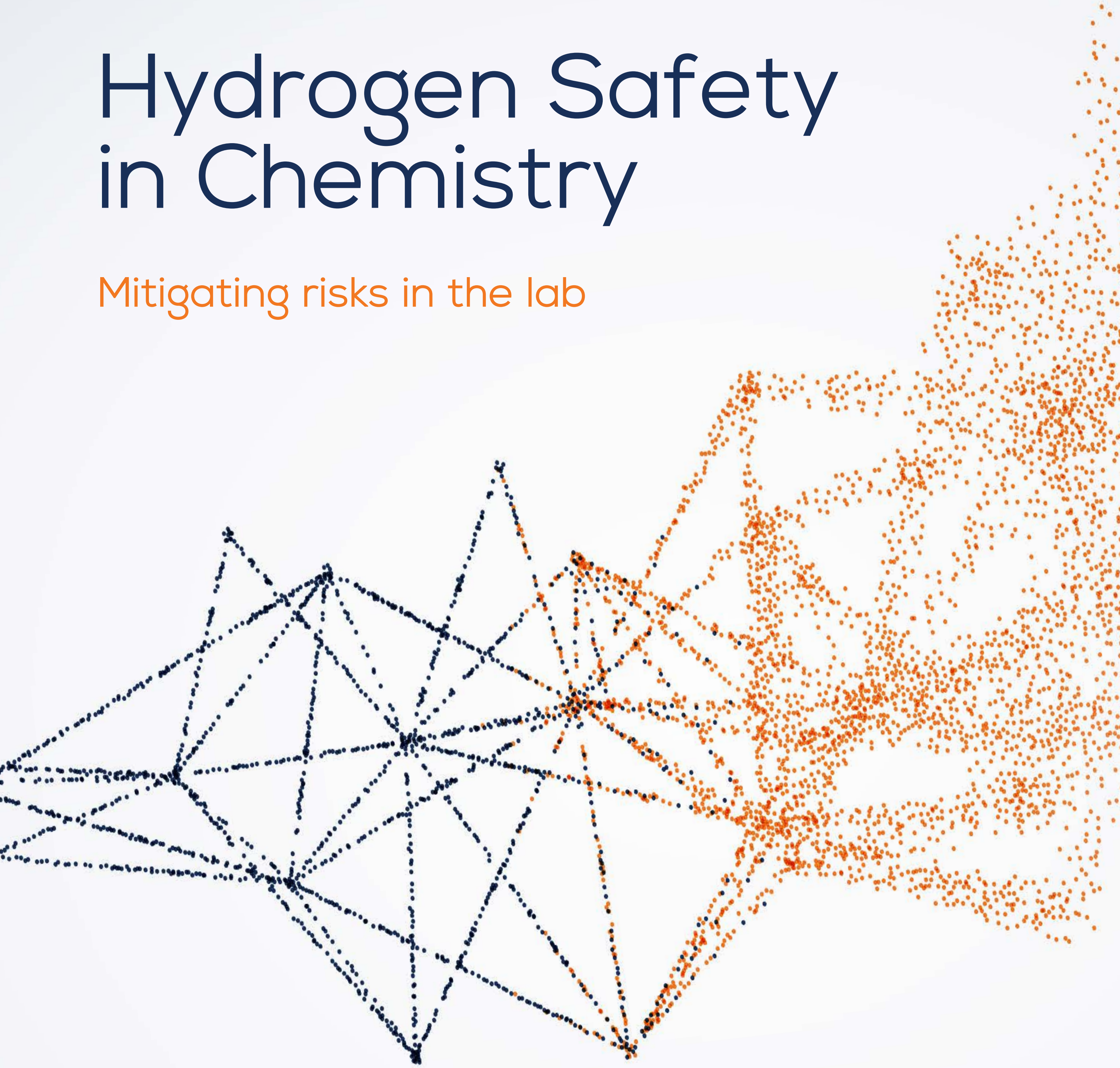
Hydrogen Safety in Chemistry

Mitigating risks in the lab



How to Reduce the Risks of Using Hydrogen in Your Lab

In this white paper, we will explore the uses of hydrogen within the chemistry world, the hazards and risks associated with hydrogen, and methods we can use to mitigate these risks. We hope that this concise paper will give you a quick overview of what must be considered when using hydrogen at your facility.

Before we get into it - a disclaimer

Following the best practices contained in this online manual represents a commitment to the safe use and handling of hydrogen, but it should be recognized that no information resource can provide 100% assurance of safety. Personnel with applicable expertise should always be consulted in designing and implementing any system carrying a potential safety risk. Additionally, since following these best practices does not guarantee compliance with local codes, standards, and regulations, users should check with their local authority having jurisdiction to ensure that those requirements are adequately addressed.

Why is hydrogen important in chemistry?

Hydrogenation

Catalytic heterogeneous hydrogenation is one of the most important and widespread techniques in the reduction of functional groups. Even with the development of homogeneous catalysis, the use of heterogeneous catalysts is still preferable and holds many advantages over their homogeneous counterparts such as easy work-up, less contamination in the products and minimizing waste. It is difficult to estimate how often hydrogenation is utilized across all chemical industries, but various sources seem to fall on an estimate of between 5-10% of all industrial reactions carried out. The importance of hydrogenation in the pharmaceutical, agrochemical, and fine chemical industry cannot be underestimated. Approximately 25% of the synthesis of marketed drugs as well as clinical drug candidates have at least one hydrogenation step in their synthetic sequence. Each of these diverse industrial hydrogenation processes started as a laboratory hydrogenation research project.

Hydrogen as a carrier gas in gas chromatography

Hydrogen is an extremely useful carrier gas for GC and provides significant benefits compared to the use of helium or nitrogen. The major benefit of hydrogen is that it can lead to a dramatic reduction of the time required for a given separation. In addition, hydrogen frequently allows for the use of a lower temperature for separation, thereby increasing column longevity. Besides its use as a carrier gas, hydrogen is used in GC as a fuel gas for flame-ionization detectors (FIDs) and as a reaction gas for Hall detectors.**(ref:** https://www.restek.com/)

Why isn't hydrogen utilized more widely?

Despite the importance of the use of hydrogen throughout the chemistry world, it is limited in its application due to the extreme flammability of hydrogen and that the hydrogen source for many laboratories around the world is the hydrogen cylinder. The main hazards associated with improper handling of gas cylinders are:

- Impact from falling cylinders;
- Manual handling injuries;
- Impact from the blast of a gas cylinder rupture or rapid release of compressed gas;
- Impact from parts of gas cylinders or valves that fail, or any flying debris;
- Fire resulting from the escape of flammable gases or fluids

In addition to this, when conducting hydrogenation, the handling and filtration of the hydrogen saturated pyrophoric catalysts, such as Raney nickel or Pd/C, in flammable solvents pose inherent safety hazards. More on these hazards later.

Safe use of hydrogen can be facilitated with the RAMP paradigm, as recommended by the American Chemical Society. (Ref: See www.acs.org/safety and www.acs.org/content/acs/en/chemical-safety/basics.html , Ref: R Hill, D Finster. Laboratory Safety for Chemistry Students, 2nd Edition, John Wiley, Hoboken, NJ, 2016)

- **R**ecognize the hazards
- **A**ssess the risk of hazards
- **M**itigate the risks
- **P**repare for emergency

The following outlines how RAMP can be applied to Lab-scale Hydrogen use.

Recognition of hazards when working with hydrogen or hydrogenation

When handling hydrogen in the lab and for hydrogenation itself, it is important to know the properties of hydrogen. Some important properties are listed in the table below.

Hydrogen	
Flammable Range:	4 – 75% v/v; almost invisible flame
Minimum Ignition Energy:	~0.02 millijoules (about 1/10 that of gasoline vapor)
Expansion Ratio (l → g):	1 → 848
JT Coefficient:	$\mu_{jt} < 0$; Hydrogen gets hot upon expansion at NTP

In particular, the flammability range of hydrogen is exceptionally broad and burns with an almost invisible flame. Couple this with a minimum ignition energy that is 1/10th that of gasoline vapor and you have a very hazardous gas that can be ignited even through a static electricity discharge. Hydrogen is unique compared to other gases in that its Joule-Thomson Coefficient is reversed (less than zero). This means that when hydrogen is released from high pressure to STP, it gets hot and not cold. The hydrogen can get so hot, that it ignites at the point of release. While asphyxiation is a concern, the major hazards are flammability and detonation. It should also be noted that hydrogen gas itself can cause metal embrittlement, which should be taken into account when designing or maintaining hydrogen systems.

Hydrogen in gas cylinders is regulated by various agencies and codes. Every country has their own. For example, in the United States, hydrogen cylinders drive OSHA and Fire Code requirements.

Namely:

- 29 CFR 1910.103 for hydrogen; 29 CFR 1910.1200 for hazard communication, and 29 CFR 1910.1450 for the Laboratory Standard
- NFPA 2, 50A & 55 for hydrogen in relation to compressed gases
- Applicable Fire Code

When looking at the risks regarding hydrogenation itself, you have to take into account all of the above hydrogen hazards, but also the hazards associated with use of pyrophoric catalysts, elevated temperature and pressure, and the chemistry itself. With regard to the chemistry, it should be investigated whether the chemistry produces any hydrogen oxidant mixtures, the potential for runaway exothermic reactions, and the presence of any unstable intermediates. Finally, also take note of the solvent you are conducting the reaction in and its potential to add any fire risk.

Assessing the risk with hydrogen/hydrogenation

Assessing the risks associated with heterogeneous catalytic hydrogenation provides the following estimates:

Failure Mode	Risk		
	Low	Moderate	High
Fire/explosion resulting from mixing with air or oxygen		■	■
Ignition by thermal runaway reaction or unstable intermediate		■	■
Catalyst ignition	■	■	
Loss of containment			■

In developing these risk assessment estimates, the frequency and consequence of each failure mode was considered. While loss of containment has a low frequency history, the results are invariably catastrophic, resulting in a **HIGH**-risk assessment.

Mitigation of Risks

How do you mitigate the risks associated with the presence and use of hydrogen?

1. Reduction in the quantity of hydrogen and elimination of hydrogen cylinders. Both can be done by utilizing a hydrogen generator. This reduces risks such as detonation, detonation intensity, fire intensity, and fire spread.
2. Catalysts risks can be mitigated by strictly following your standard operating procedure (SOP) for catalyst handling. This reduces the risk of sparking, fire frequency, and fire intensity.

3. Risks associated with loss of containment can be mitigated by proper inspection and installation of the pipes and fittings, use of well-trained personnel, and high-level supervision. Reduction of the amount of hydrogen will also reduce risk of loss of containment, such as only producing hydrogen on demand through a hydrogen generator.

With these mitigation approaches implemented, the previous risk assessment is modified with the following results.

Failure Mode	Risk		
	Low	Moderate	High
Fire/explosion resulting from mixing with air or oxygen			
Ignition by thermal runaway reaction or unstable intermediate			
Catalyst ignition			
Loss of containment			

There is a rich body of literature regarding the handling of hydrogen. Some highlighted references are given below:

- R Hill, D Finster. Laboratory Safety for Chemistry Students, 2nd Edition, John Wiley, Hoboken, NJ, 2016
- Development of a Modeling-Based Strategy for the Safe and Effective Scale-up of Highly Energetic Hydrogenation Reactions, Mitchell, Christopher W.; Strawser, Josiah D.; Gottlieb, Alex; Millonig, Michael H.; Hicks, Frederick A.; Papageorgiou, Charles D. Organic Process Research & Development (2014), 18(12), 1828-1835.
- Sequential Nitration/Hydrogenation Protocol for the Synthesis of Triaminophloroglucinol: Safe Generation and Use of an Explosive Intermediate under Continuous-Flow Conditions, Cantillo, David; Damm, Markus; Dallinger, Doris; Bauser, Marcus; Berger, Markus; Kappe, C. Oliver, Organic Process Research & Development (2014), 18(11), 1360-1366.
- Dangerous Gas Mixtures: Avoiding Cylinder Accidents, Eugene Ngai, www.specialtygasreport.com, 2014

What to do in a hydrogen-related emergency:

Hydrogen Leak Detected

1. Evacuate the immediate area of all personnel.
2. Shut off the hydrogen source immediately and vent all hydrogen to a safe outside location.
3. Increase indoor ventilation with emergency explosion-proof exhaust fans, if possible.
4. Initiate the local emergency plan and make the required emergency contacts.

Hydrogen fire/explosion

In the unfortunate event that a hydrogen fire or explosion does occur, it is essential that you have good lab practices and well-trained personnel in how to deal with such an emergency. However, in short:

- Your number one priority are your people and ensuring that they are safe. Evacuate the area
- The first thing to do when confronted with the fire is to assess the situation and shut-off the source of the hydrogen **IF SAFE TO DO SO.** If this can be done remotely then all the better. You cannot extinguish the fire until the source has been shut off. This will limit any further danger and damage. If it is not safe to do so, such as with a hydrogen cylinder leak in a lab environment, then evacuate immediately and let the fire services handle it.
- Ensure you have the back-up both from an internal and external standpoint. Have the fire and ambulance services been notified? Provide the fire services with as much detail as possible regarding the incident including hazardous material (including hydrogen) inventories and locations, facility safety equipment and instrumentation, and any actions taken so far.

In terms of what to do, there is an extensive detailed list of actions and other information regarding hydrogen safety at the following website: https://h2tools.org/

Specific Risk Mitigation Solutions

When looking at the risks of hydrogen as a whole, good lab practices and well-trained personnel are essential in mitigating this. Removal of hydrogen cylinders and replacing them with hydrogen generators solves a lot of the issues. At ThalesNano Energy, we developed the H-Genie®, a high-pressure capable hydrogen generator that enables chemists to utilize hydrogen in a safe and smart way for their chemistry.

How does the H-Genie® work and help chemists with hydrogen?

The H-Genie® is the first hydrogen generator designed specifically for chemistry and the chemistry laboratory. It works by generating hydrogen gas up to 100 bar (1450psi) and 4.0 purity from deionized water using a patented high-pressure electrolytic cell. The H-Genie® is designed to supply high purity hydrogen gas to hydrogen balloons, autoclave or bomb reactors, and flow reactors.

The following is a list of safety benefits designed in the system that outline how safety can be improved by modernizing your lab and utilizing hydrogen generators over cylinders:

- Hydrogen gas is generated from deionized water "on demand", so there is no stored hydrogen thereby reducing explosion or fire risk. Most regulatory requirements associated with hydrogen use and storage are markedly reduced.
- The internal volume of the H-Genie® is less than 150 cm^3. An average size lab hydrogen cylinder will have 1000s of compressed liters. e.g. a 50L volume cylinder will have 5000L at 100 bar (1450 psi). This is over 300 times more volume of hydrogen than the H-Genie® at 100 bar. Again, this substantially reduces the risk of fire or explosion.
- If a fire breaks out in the building, then the electricity is usually turned off. When the electricity is turned off, the H-Genie® will no longer produce hydrogen (if it is working at the time). In a fire a cylinder can overheat and fail, releasing the entire hydrogen gas contents.

- The H-Genie® is equipped with an internal hydrogen sensor, so in the unlikely event of a hydrogen leak the system will automatically shut down.
- If the H-Genie® cannot generate hydrogen pressure internally (i.e. there is a gas leak), then the system will automatically go into emergency shutdown mode.
- Water leak detection at the base of the instrument.
- Ventilation of the interior of the H-Genie® using 3 fans ensures that the temperature inside the unit does not rise excessively and prevents accumulation of hydrogen or oxygen in the event of a leak.
- Upon power-up the H-Genie® performs a self-check for internal leaks.
- The hydrogen pressure inside the generator should only reach a maximum of 115 bar (1668 psi) and this is controlled electronically via a pressure sensor and mechanically using a pressure relief valve (Fail Safe).
- When the H-Genie® is in emergency status the following occurs:
    - The current to the cell is stopped.
    - The internally stored hydrogen is evacuated into the fume hood.
    - An audible and visual alarm will be heard

In addition to the safety aspects, the ability to simplify or improve chemistry capability in the lab is equally important. Here are a set of unique features that are provided specifically to help chemists.

- Pressure capability: The H-Genie® provides a minimum ten times (10) higher hydrogen gas pressure when compared to competitor technology to increase reaction rates and widen the number the of functional groups you can react.
- Hydrogen consumption monitoring
- Batch AND flow reactor compatibility
- Remote operation and reaction data export.

We believe that hydrogen generators are the future for utilizing gases in laboratories.

For more information on the H-Genie®

contact us at sales@thsenergy.com

ThalesNano energy