MODULE 1:

Hydrogen Properties

College of the Desert

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MODULE 1: HYDROGEN PROPERTIES

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OBJECTIVES

At the completion of this module, the technician will understand:

- the atomic structure of hydrogen
- the physical and chemical properties of hydrogen
- how hydrogen compares to hydrocarbon fuels in terms of energy, flammability and safety
- the fundamental gas laws
- how pressure, temperature and mass flow are measured
- the units of pressure, temperature, volume, mass and mass flow as they relate to gases

MODULE 1: HYDROGEN PROPERTIES

Key Points & Notes

1.1 Atomic Structure

Hydrogen is by far the most plentiful element in the universe, making up 75% of the mass of all visible matter in stars and galaxies.

Hydrogen is the simplest of all elements. You can visualize a hydrogen atom as a dense central nucleus with a single orbiting electron, much like a single planet in orbit around the sun. Scientists prefer to describe the electron as occupying a "probability cloud" that surrounds the nucleus somewhat like a fuzzy, spherical shell.

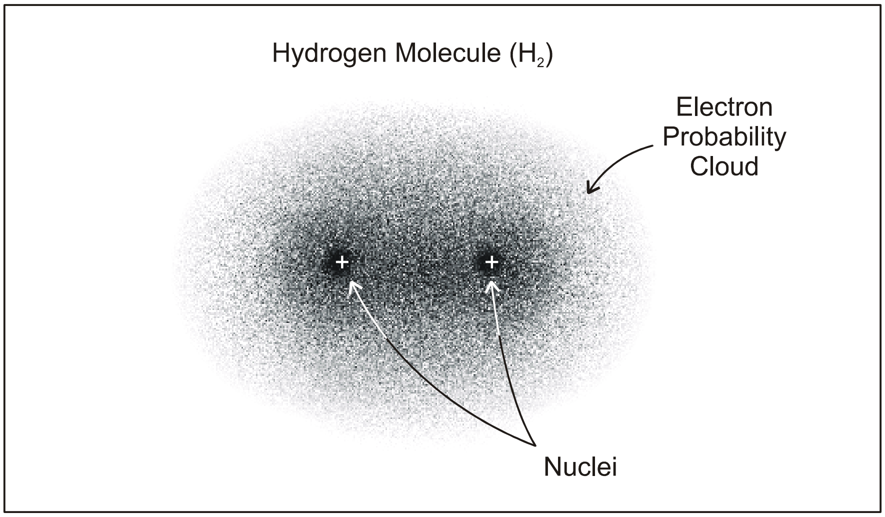


Figure 1-1 Atomic Structure of a Hydrogen Molecule

In most hydrogen atoms, the nucleus consists of a single proton, although a rare form (or "isotope") of hydrogen contains both a proton and a neutron. This form of hydrogen is called deuterium or heavy hydrogen. Other isotopes of hydrogen also exist, such as tritium with two neutrons and one proton, but these isotopes are unstable and decay radioactively.

Most of the mass of a hydrogen atom is concentrated in its nucleus. In fact, the proton is more than 1800 times more massive than the electron. Neutrons have almost the same mass as protons. However, the radius of the electron's orbit, which defines the size of the atom, is approximately 100,000 times as large as the radius of the nucleus! Clearly, hydrogen atoms consist largely of empty space. Atoms of all elements consist largely of empty space, although all others are heavier and have more electrons.

A proton has a positive electrical charge, and an electron has a negative electrical charge. Neutrons do not carry a charge.

Key Points & Notes

Together, the charges associated with the proton and electron of each hydrogen atom cancel each other out, so that individual hydrogen atoms are electrically neutral.

Chemically, the atomic arrangement of a single electron orbiting a nucleus is highly reactive. For this reason, hydrogen atoms naturally combine into molecular pairs (H_2 instead of H). To further complicate things, each proton in a hydrogen pair has a field associated with it that can be visualized and described mathematically as a “spin”. Molecules in which both protons have the same spin are known as “orthohydrogen”. Molecules in which the protons have opposite spins are known as “parahydrogen”.

Over 75% of normal hydrogen at room temperature is orthohydrogen. This difference becomes important at very low temperatures since orthohydrogen becomes unstable and changes to the more stable parahydrogen arrangement, releasing heat in the process. This heat can complicate low temperature hydrogen processes, particularly liquefaction.

Composition of Other Fuels

It is natural for us to compare hydrogen to other hydrocarbon fuels with which we are more familiar. All hydrocarbon fuels are molecular combinations of carbon and hydrogen atoms. There are thousands of types of hydrocarbon compounds, each with a specific combination of carbon and hydrogen atoms in a unique geometry.

The simplest of all hydrocarbons is methane, which is the principal constituent of natural gas. (Other components of natural gas include ethane, propane, butane and pentane as well as impurities.) Methane has the chemical formula CH_4, which means that each molecule has four hydrogen atoms and one carbon atom.

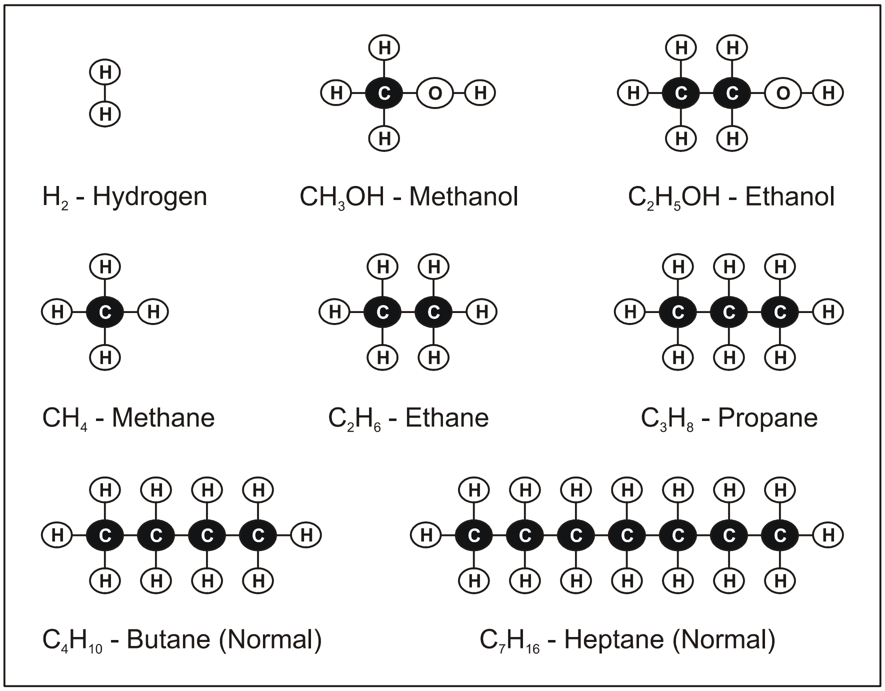
Other common hydrocarbons are ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}). These are all considered light hydrocarbons since they contain less than five carbon atoms per molecule and therefore have low molecular weight (a carbon atom is almost 12 times as heavy as a hydrogen atom).

Gasoline is composed of a mixture of many different hydrocarbons, but an important constituent is heptane (C_7H_{16}). Gasoline, diesel, kerosene, and compounds found in asphalt, heavy oils and waxes, are considered heavy hydrocarbons as they contain many carbon atoms per molecule, and therefore have high molecular weight.

Key Points & Notes

The lightest hydrocarbons are gases at normal atmospheric pressure and temperature. Heavier hydrocarbons, with 5 to 18 carbon atoms per compound, are liquid at ambient conditions and have increasing viscosity with molecular weight.

Other chemical fuels include alcohols whose molecules combine an oxygen/hydrogen atom pair (OH) with one or more hydrocarbon groups. Common alcohol fuels are methanol (CH_3OH) and ethanol (C_2H_5OH). These may be blended with hydrocarbons for use in internal combustion engines.



H_2 - Hydrogen

CH_3OH - Methanol

C_2H_5OH - Ethanol

CH_4 - Methane

C_2H_6 - Ethane

C_3H_8 - Propane

C_4H_{10} - Butane (Normal)

C_7H_{16} - Heptane (Normal)

Figure 1-2 Chemical Structure of Common Fuels

1.2 Physical Properties

1.2.1 State

All substances exist on earth as either a gas, liquid or solid. Most substances will change from one of these states to another depending on the temperature and pressure of their surroundings. In general, a gas can be changed into a liquid by reducing its temperature, and a liquid to a solid by reducing its temperature further. To some extent, an increase in pressure will cause a substance to liquefy and solidify at higher temperature than would otherwise be required.

The transition from liquid to gas is known as boiling and the transition from liquid to solid as freezing. Accordingly, each substance has a characteristic boiling temperature and freezing temperature (at a given pressure). The opposite transitions, from gas to liquid and solid to liquid, are known as condensation and melting respectively. The condensation temperature is the same as the boiling temperature and the melting temperature is the same as the freezing temperature. The process of condensation is also known as liquefaction and the process of freezing is also known as solidification.

Boiling and freezing temperatures are most meaningfully compared relative to “absolute zero”. Absolute zero (0 °R; 0 K; –459.69 °F; –273.15 °C) is the lowest temperature in the universe at which all molecular motion stops.

Hydrogen has the second lowest boiling point and melting points of all substances, second only to helium. Hydrogen is a liquid below its boiling point of 20 K (–423 °F; –253 °C) and a solid below its melting point of 14 K (–434 °F; –259 °C) and atmospheric pressure.

Obviously, these temperatures are extremely low. Temperatures below –100 °F (200 K; –73 °C) are collectively known as cryogenic temperatures, and liquids at these temperatures are known as cryogenic liquids.

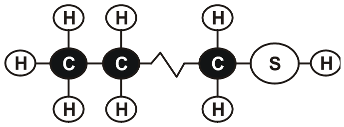
The boiling point of a fuel is a critical parameter since it defines the temperature to which it must be cooled in order to store and use it as a liquid. Liquid fuels take up less storage space than gaseous fuels, and are generally easier to transport and handle. For this reason, fuels that are liquid at atmospheric conditions (such as gasoline, diesel, methanol and ethanol) are particularly convenient. Conversely, fuels that are gases at atmospheric conditions (such as hydrogen and natural gas) are less convenient as they must be stored as a pressurized gas or as a cryogenic liquid.

The boiling point of a pure substance increases with applied pressure—up to a point. Propane, with a boiling point of –44 °F (–42 °C), can be stored as a liquid under moderate pressure, although it is a gas at atmospheric pressure. (At temperatures of 70 °F (21 °C) a minimum pressure of 111 psig (7.7 barg) is required for liquefaction). Unfortunately, hydrogen's boiling point can only be increased to a maximum of -400 °F (–240 °C) through the application of approximately 195 psig (13 barg), beyond which additional pressure has no beneficial effect.

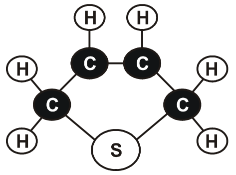
Hydrogen as a vehicle fuel can be stored either as a high-pressure gas or as a cryogenic liquid (Section 2.2).

1.2.2 Odor, Color and Taste

Pure hydrogen is odorless, colorless and tasteless. A stream of hydrogen from a leak is almost invisible in daylight. Compounds such as mercaptans and thiophanes that are used to scent natural gas may not be added to hydrogen for fuel cell use as they contain sulfur that would poison the fuel cells.



Mercaptan



Thiophane

Hydrogen that derives from reforming other fossil fuels (Section 2.1.2) is typically accompanied by nitrogen, carbon dioxide, carbon monoxide and other trace gases. In general, all of these gases are also odorless, colorless and tasteless.

1.2.3 Toxicity

Hydrogen is non-toxic but can act as a simple asphyxiant by displacing the oxygen in the air.

Asphyxiation

Oxygen levels below 19.5% are biologically inactive for humans. Effects of oxygen deficiency may include rapid breathing, diminished mental alertness, impaired muscular coordination, faulty judgement, depression of all sensations, emotional instability and fatigue. As asphyxiation progresses, dizziness, nausea, vomiting, prostration and loss of consciousness may result, eventually leading to convulsions, coma and death. At concentrations below 12%, immediate unconsciousness may occur with no prior warning symptoms.

In an enclosed area, small leaks pose little danger of asphyxiation whereas large leaks can be a serious problem since the hydrogen diffuses quickly to fill the volume. The potential for asphyxiation in unconfined areas is almost negligible due to the high buoyancy and diffusivity of hydrogen.

Inhaled hydrogen can result in a flammable mixture within the body. Inhaling hydrogen can lead to unconsciousness and asphyxiation.

Other Gases Accompanying Hydrogen

Gases that accompany hydrogen when reforming other fossil fuels, such as nitrogen, carbon dioxide, carbon monoxide and other trace gases, can also act as asphyxiants by displacing oxygen. In addition, carbon monoxide is a poisonous gas that is a severe health hazard.

Carbon Monoxide

The affinity of hemoglobin (in the blood) for carbon monoxide is 200–300 times greater than its affinity for oxygen. As a result, inhalation of carbon monoxide quickly restricts the amount of oxygen in the bloodstream and asphyxiation ensues. Asphyxiation can continue for some time after a victim is moved to fresh air.

Depending on levels and duration of exposure, the symptoms may include headache, dizziness, heart palpitations, weakness, confusion, or nausea, leading to convulsions, eventual unconsciousness and death. With repeated long-term overexposures, carbon monoxide can damage the central nervous system and possibly lead to hardening of arteries. Since carbon monoxide is odorless, colorless and tasteless, there is no warning of its presence other than the symptoms it causes.

Published exposure limits vary somewhat depending on the regulating body. Typical values state that exposure to carbon monoxide becomes a health hazard when it exceeds the time weighted average of 25 molar ppm over 8 hours, or 100 molar ppm over 15 minutes. An exposure of 1200 ppm poses immediate danger without warning symptoms.

Carbon monoxide is poisonous.

Carbon monoxide is flammable over a very wide range of concentrations in air (12.5 – 74%). As a result, even small leaks of carbon monoxide have the potential to burn or explode. Leaked carbon monoxide can concentrate in an enclosed environment, thereby increasing the risk of combustion and explosion. The autoignition temperature of carbon monoxide is 609 °C (1128 °F). Carbon monoxide has almost the same density as air and will therefore not diffuse by rising. Carbon monoxide burns with a characteristic blue flame.

A mixture of carbon monoxide and air is potentially flammable and explosive, and can be ignited by a spark or hot surface!

1.2.4 Density and Related Measures

Hydrogen has lowest atomic weight of any substance and therefore has very low density both as a gas and a liquid.

Density

Density is measured as the amount of mass contained per unit volume. Density values only have meaning at a specified temperature and pressure since both of these parameters affect the compactness of the molecular arrangement, especially in a gas. The density of a gas is called its vapor density, and the density of a liquid is called its liquid density.

Substance	Vapor Density (at 68 ºF; 20 ºC, 1 atm)	Liquid Density (at normal boiling point, 1 atm)
Hydrogen	0.005229 lb/ft^3 (0.08376 kg/m^3)	4.432 lb/ft^3 (70.8 kg/m^3)
Methane	0.0406 lb/ft^3 (0.65 kg/m^3)	26.4 lb/ft^3 (422.8 kg/m^3)
Gasoline	0.275 lb/ft^3 (4.4 kg/m^3)	43.7 lb/ft^3 (700 kg/m^3)

Table 1-2 Vapor and Liquid Densities of Comparative Substances

Specific Volume

Specific volume is the inverse of density and expresses the amount of volume per unit mass. Thus, the specific volume of hydrogen gas is 191.3 ft^3/lb (11.9 m^3/kg) at 68 °F (20 °C) and 1 atm, and the specific volume of liquid hydrogen is 0.226 ft^3/lb (0.014 m^3/kg) at –423 °F (–253 °C) and 1 atm.

Specific Gravity

A common way of expressing *relative* density is as specific gravity. Specific gravity is the ratio of the density of one substance to that of a reference substance, both at the same temperature and pressure.

For vapors, air (with a density of 0.0751 lb/ft^3; 1.203 kg/m^3) is used as the reference substance and therefore has a specific gravity of 1.0 relative to itself. The density of other vapors are then expressed as a number greater or less than 1.0 in proportion to its density relative to air. Gases with a specific gravity greater than 1.0 are heavier than air; those with a specific gravity less than 1.0 are lighter than air.

Gaseous hydrogen, with a density of 0.00523 lb/ft^3, has a specific gravity of 0.0696 and is thus approximately 7% the density of air.

For liquids, water (with a density of 62.4 lb/ft^3; 1000 kg/m^3) is used as the reference substance, so has a specific gravity of 1.0 relative to itself. As with gases, liquids with a specific gravity greater than 1.0 are heavier than water; those with a specific gravity less than 1.0 are lighter than water.

Liquid hydrogen, with a density of 4.432 lb/ft^3, has a specific gravity of 0.0708 and is thus approximately (and coincidentally) 7% the density of water.

Expansion Ratio

The difference in volume between liquid and gaseous hydrogen can easily be appreciated by considering its expansion ratio. Expansion ratio is the ratio of the volume at which a gas or liquid is stored compared to the volume of the gas or liquid at atmospheric pressure and temperature.

When hydrogen is stored as a liquid, is vaporizes upon expansion to atmospheric conditions with a corresponding increase in volume. Hydrogen's expansion ratio of 1:848 means that hydrogen in its gaseous state at atmospheric conditions occupies 848 times more volume than it does in its liquid state.

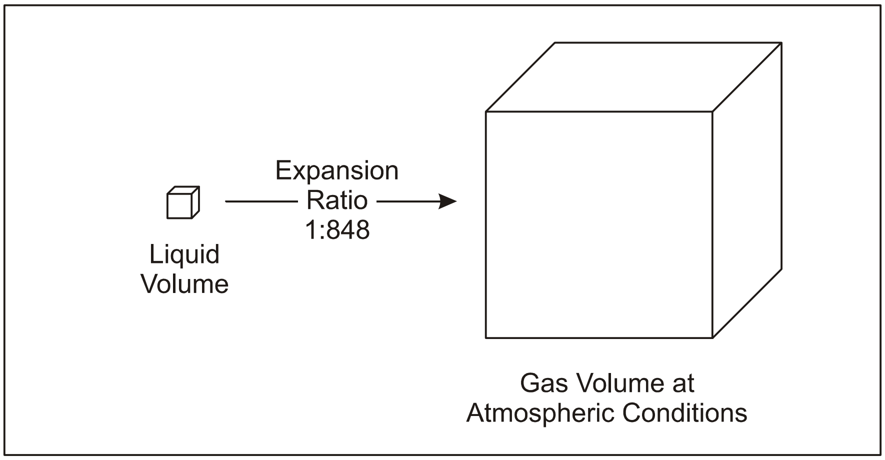


Figure 1-3 Hydrogen Liquid to Gas Expansion Ratio

When hydrogen is stored as a high-pressure gas at 3600 psig (250 barg) and atmospheric temperature, its expansion ratio to atmospheric pressure is 1:240. While a higher storage pressure increases the expansion ratio somewhat, gaseous hydrogen under any conditions cannot approach the expansion ratio of liquid hydrogen.

Hydrogen Content

Key Points & Notes

Even as a liquid, hydrogen is not very dense. Ironically, every cubic meter of water (made up of hydrogen and oxygen) contains 111 kg of hydrogen whereas a cubic meter of liquid hydrogen contains only 71 kg of hydrogen. Thus, water packs more mass of hydrogen per unit volume, because of its tight molecular structure, than hydrogen itself. This is true of most other liquid hydrogen-containing compounds as well; a cubic meter of methanol contains 100 kg of hydrogen and a cubic meter of heptane contains 113 kg. Hydrocarbons are compact hydrogen carriers with the added advantage of having higher energy density than pure hydrogen (Section 1.3.1.2).

When used as vehicle fuel, the low density of hydrogen necessitates that a large volume of hydrogen be carried to provide an adequate driving range.

1.2.5 Leakage

The molecules of hydrogen gas are smaller than all other gases, and it can diffuse through many materials considered airtight or impermeable to other gases. This property makes hydrogen more difficult to contain than other gases.

Leaks of liquid hydrogen evaporate very quickly since the boiling point of liquid hydrogen is so extremely low.

Hydrogen leaks are dangerous in that they pose a risk of fire where they mix with air (Section 1.3.1). However, the small molecule size that increases the likelihood of a leak also results in very high buoyancy and diffusivity, so leaked hydrogen rises and becomes diluted quickly, especially outdoors. This results in a very localized region of flammability that disperses quickly. As the hydrogen dilutes with distance from the leakage site, the buoyancy declines and the tendency for the hydrogen to continue to rise decreases. Very cold hydrogen, resulting from a liquid hydrogen leak, becomes buoyant soon after is evaporates.

In contrast, leaking gasoline or diesel spreads laterally and evaporates slowly resulting in a widespread, lingering fire hazard. Propane gas is denser than air so it accumulates in low spots and disperses slowly, resulting in a protracted fire or explosion hazard. Heavy vapors can also form vapor clouds or plumes that travel as they are pushed by breezes. Methane gas is lighter than air, but not nearly as buoyant as hydrogen, so it disperses rapidly, but not as rapidly as hydrogen.

For small hydrogen leaks, buoyancy and diffusion effects in air are often overshadowed by the presence of air currents from a slight ambient wind, very slow vehicle motion or the radiator fan. In general, these currents serve to disperse leaked hydrogen even more quickly with a further reduction of any associated fire hazard.

When used as vehicle fuel, the propensity for hydrogen to leak necessitates special care in the design of the fuel system to ensure that any leaks can disperse with minimum hindrance, and the use of dedicated leak detection equipment on the vehicle and within the maintenance facility.

Hydrogen leaks pose a potential fire hazard.

Key Points & Notes

Gasoline Leak

Liquid Propane Leak

Liquid Hydrogen Leak

Courtesy Michael Swain/U.S. DOT

Figure 1-4 Fuel Leak Simulations

1.3 Chemical Properties

1.3.1 Reactivity

High reactivity is characteristic of all chemical fuels. In each case, a chemical reaction occurs when the fuel molecules form bonds with oxygen (from air) so that the final, reacted molecules are at a lower energy state than the initial, unreacted molecules.

As the molecules react, the change in chemical energy state is accompanied by a corresponding release of energy that we can exploit to do useful work. This is true in both a combustive reaction (as in an internal combustion engine where the energy is released explosively as heat) or in an electrochemical reaction (as in a battery or fuel cell where the energy is released as an electrical potential and heat).

This chemical energy release is analogous to that which occurs when water flows from a high level to a low level. The water at the high level has potential energy that is released as it falls to the low level. This energy can be harnessed to do useful work, such as turning a turbine.

Once at the low level, the energy is spent and it cannot do further work at that level. In order to do further work, it must either fall to an even lower level, or be raised back to the high level through some external agency that inputs energy. The natural cycle of evaporation, condensation, and precipitation that returns water to a higher level is driven by solar and wind energy. Alternatively, a pump can return the water to a higher level, but the pump consumes a corresponding amount of energy.

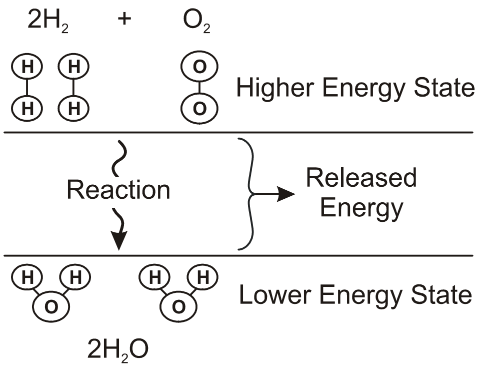


Figure 1-5 Chemical Energy States

Chemical reactions of this type often require a small amount of activation energy to get started, but then the energy re-

Key Points & Notes

leased by the reaction feeds further reaction in a domino effect. Thus, when a small amount of activation energy in the form of a spark is provided to a mixture of hydrogen and oxygen, the molecules react vigorously, releasing a substantial amount of heat, with water as the final product. We experience this reaction as a fire or explosion, and the resulting water vaporizes and is invisible to us since it is a superheated vapor. (This water vapor can condense and become visible as it cools; this is the cloud we see when the space shuttle takes off.)

The water-forming reaction of hydrogen and oxygen is reversible. Thus, it is possible to convert water, at a low energy state, to hydrogen and oxygen, at a higher energy state, by adding energy slightly greater than that which was previously released (the extra to cover losses). This is the principle behind hydrogen production through electrolysis (Section 2.1.1).

Chemical By-Products of Fuel Reactions

All of the atoms present at the start of a reaction are present at the end of the reaction although they may be reorganized into different molecules. Hydrocarbon fuels, in addition to hydrogen and carbon, may contain other impurities such as sulfur. Air, in addition to being a ready source of oxygen, also consists of 78% nitrogen and 1% trace gases.

The presence of carbon, nitrogen and sulfur (as well as unreacted hydrocarbons) result in chemical compounds during combustion that cause smog with serious health and environmental consequences:

- Oxygen reacts with carbon to form carbon monoxide (CO) and carbon dioxide (CO_2). CO_2 is benign to human beings and does not produce smog, but is a greenhouse gas and contributes to global warming. CO, on the other hand, is poisonous to humans and severely limits the blood's ability to transport oxygen to body tissues resulting in dizziness, headaches, impaired coordination and death. The formation of CO is favored by lack of air during combustion and therefore leaner running engines emit less CO. Any reduction in CO formation is accompanied by a proportional increase in CO_2 formation.
- Oxygen reacts with nitrogen to form oxides of nitrogen (NOx). Oxides of nitrogen damage lung tissue and act as a precursor to ozone, which irritates the respiratory tract and eyes, decreases the lungs' ability to work, and causes both cough and chest pain. The formation of NOx is favored by high combustion temperatures (2700 °F; 1480

> *"In the United States, emissions from 190 million cars, trucks and buses account for half of all air pollution – more than 80% in major cities – and one-third of carbon dioxide emissions"*
>
> *— American Methanol Institute, 1998*

°C); thus, advanced ignition and increased pressure ratios tend to increase NOx emissions since these increase the combustion temperature. Lean burning engines typically reduce NOx emissions. Diesel engines, however, generate high NOx emissions when operating lean under low load conditions.

- Oxygen reacts with sulfur to form oxides of sulfur (SOx). Sulfur also forms the basis for soot, which is a form of particulate matter. Large soot particles are visible and can be filtered out of the air, or coughed out of the respiratory system. Very small soot particles (<2.5 microns) are not visible and can lodge in the lungs and cause cancer.
- Hydrocarbon emissions pass into the atmosphere through incomplete combustion and evaporation. Hydrocarbons are either volatile organic compounds (VOC's) or reactive hydrocarbons (RHC). The RHC's, such as gasoline, produce photochemical smog (visual pollution). VOC's, such as natural gas, do not produce smog. Unburned hydrocarbons act as precursor to ozone just like NOx emissions.

The type of fuel and the use of post-combustion catalytic converters affect the amount and type of smog pollution. Light hydrocarbons are relatively rich in hydrogen and therefore provide less carbon atoms for CO and CO_2 formation. Non-sulfur containing fuels eliminate SOx and soot.

Hydrogen is a nearly ideal fuel in terms of smog reduction when combusted. Hydrogen contains no carbon or sulfur, so no CO, CO_2 or SOx or soot is produced during combustion (although the combustion of lubricating oil may result in trace amounts). Hydrogen allows for leaner combustion, resulting in lower combustion temperatures and very low NOx emissions. Hydrogen is non-toxic so uncombusted hydrogen does not pose a direct health risk.

Hydrogen is an ideal fuel in terms of smog reduction when used electrochemically in a fuel cell, rather than combusted. Hydrogen in a fuel cell produces zero harmful emissions. Oxides of nitrogen are completely eliminated due to the low operating temperature (175 °F; 80 °C) of the cells. Lubricating oil is not present and is therefore not reacted.

1.3.2 Energy

Energy Content

Every fuel can liberate a fixed amount of energy when it reacts completely with oxygen to form water. This energy

Key Points & Notes

Use of hydrogen in the U.S. transportation sector alone could reduce 70% of CO emissions, 41% of NOx emissions, 38% of hydrocarbon emissions, and 30% of human-generated CO2 emissions.

content is measured experimentally and is quantified by a fuel's higher heating value (HHV) and lower heating value (LHV). The difference between the HHV and the LHV is the "heat of vaporization" and represents the amount of energy required to vaporize a liquid fuel into a gaseous fuel, as well as the energy used to convert water to steam.

The higher and lower heating values of comparative fuels are indicated in Table 1-3. Although the terms HHV and LHV do not apply to batteries, the energy density of a lead acid battery is approximately 46 Btu/lb (0.108 kJ/g).

Fuel	Higher Heating Value (at 25 ºC and 1 atm)	Lower Heating Value (at 25 ºC and 1 atm)
Hydrogen	61,000 Btu/lb (141.86 kJ/g)	51,500 Btu/lb (119.93 kJ/g)
Methane	24,000 Btu/lb (55.53 kJ/g)	21,500 Btu/lb (50.02 kJ/g)
Propane	21,650 Btu/lb (50.36 kJ/g)	19,600 Btu/lb (45.6 kJ/g)
Gasoline	20,360 Btu/lb (47.5 kJ/g)	19,000 Btu/lb (44.5 kJ/g)
Diesel	19,240 Btu/lb (44.8 kJ/g)	18,250 Btu/lb (42.5 kJ/g)
Methanol	8,580 Btu/lb (19.96 kJ/g)	7,760 Btu/lb (18.05 kJ/g)

Table 1-3 Heating Values of Comparative Fuels

Gaseous fuels are already vaporized so no energy is required to convert them to a gas. The water that results from both a combustive reaction and the electrochemical reaction within a fuel cell occurs as steam, therefore the lower heating value represents the amount of energy available to do external work.

Both the higher and lower heating values denote the amount of energy (in Btu's or Joules) for a given *weight* of fuel (in pounds or kilograms). Hydrogen has the highest energy-to-weight ratio of any fuel since hydrogen is the lightest element and has no heavy carbon atoms. It is for this reason that hydrogen has been used extensively in the space program where weight is crucial.

Specifically, the amount of energy liberated during the reaction of hydrogen, on a mass basis, is about 2.5 times the heat of combustion of common hydrocarbon fuels (gasoline, diesel, methane, propane, etc.) Therefore, for a given load duty, the mass of hydrogen required is only about a third of the mass of hydrocarbon fuel needed.

The high energy content of hydrogen also implies that the energy of a hydrogen gas explosion is about 2.5 times that of common hydrocarbon fuels. Thus, on an equal mass basis,

Key Points & Notes

Hydrogen Explosion

Key Points & Notes

hydrogen gas explosions are more destructive and carry further. However, the duration of a conflagration tends to be inversely proportional to the combustive energy, so that hydrogen fires subside much more quickly than hydrocarbon fires.

Energy Density

Whereas the energy content denotes the amount of energy for a given *weight* of fuel, the energy density denotes the amount of energy (in Btu's or Joules) for a given *volume* (in ft^3 or m^3) of fuel. Thus, energy density is the product of the energy content (LHV in our case) and the density of a given fuel.

The energy density is really a measure of how compactly hydrogen atoms are packed in a fuel. It follows that hydrocarbons of increasing complexity (with more and more hydrogen atoms per molecule) have increasing energy density. At the same time, hydrocarbons of increasing complexity have more and more carbon atoms in each molecule so that these fuels are heavier and heavier in absolute terms.

On this basis, hydrogen's energy density is poor (since it has such low density) although its energy to *weight* ratio is the best of all fuels (because it is so light). The energy density of comparative fuels, based on the LHV, is indicated in Table 1-4. The energy density of a lead acid battery is approximately 8700 Btu/ft^3 (324,000 kJ/m^3).

Fuel	Energy Density (LHV)
Hydrogen	270 Btu/ft^3 (10,050 kJ/m^3); gas at 1 atm and 60 ºF (15 ºC) 48,900 Btu/ft^3 (1,825,000 kJ/m^3); gas at 3,000 psig (200 barg) and 60 ºF (15 ºC) 121,000 Btu/ft^3 (4,500,000 kJ/m^3); gas at 10,000 psig (690 barg) and 60 ºF (15 ºC) 227,850 Btu/ft^3 (8,491,000 kJ/m^3); liquid
Methane	875 Btu/ft^3 (32,560 kJ/m^3); gas at 1 atm and 60 ºF (15 ºC) 184,100 Btu/ft^3 (6,860,300 kJ/m^3); gas at 3,000 psig (200 barg) and 60 ºF (15 ºC) 561,500 Btu/ft^3 (20,920,400 kJ/m^3); liquid
Propane	2,325 Btu/ft^3 (86,670 kJ/m^3); gas at 1 atm and 60 ºF (15 ºC) 630,400 Btu/ft^3 (23,488,800 kJ/m^3); liquid
Gasoline	836,000 Btu/ft^3 (31,150,000 kJ/m^3); liquid
Diesel	843,700 Btu/ft^3 (31,435,800 kJ/m^3) minimum; liquid
Methanol	424,100 Btu/ft^3 (15,800,100 kJ/m^3); liquid

Table 1-4 Energy Densities of Comparative Fuels

Key Points & Notes

The energy density of a fuel is also affected by whether the fuel is stored as a liquid or as a gas, and if a gas, at what pressure. To put it into perspective:

- A 132-gal (500-L) diesel tank containing 880 lb (400 kg) of fuel is equivalent on an energy basis to a 2110 gal (8000 L) volume of hydrogen gas at 3600 psi (250 barg). This is a 16 times increase in volume, although the weight of the hydrogen is only 330 lb (150 kg), representing a decrease in fuel weight by a factor of about 2.8.
- The same diesel tank is equivalent to a 550-gal (2100-L) tank of liquid hydrogen. This is a 4.2 times increase in volume.
- If hydrogen is stored as a metal hydride, every kilogram of diesel fuel is replaced by approximately 4.5 kg of metal hydride to maintain the same hydrogen/diesel energy equivalence. Thus the same 132 gal (500 L) diesel tank containing 880 lb (400 kg) of fuel would have to be replaced with a hydride tank containing 3800 lb (1725 kg) of “fuel” mass.

1.3.3 Flammability

Three things are needed for a fire or explosion to occur: a fuel, oxygen (mixed with the fuel in appropriate quantities) and a source of ignition. Hydrogen, as a flammable fuel, mixes with oxygen whenever air is allowed to enter a hydrogen vessel, or when hydrogen leaks from any vessel into the air. Ignition sources take the form of sparks, flames, or high heat.

Flashpoint

All fuels burn only in a gaseous or vapor state. Fuels like hydrogen and methane are already gases at atmospheric conditions, whereas other fuels like gasoline or diesel that are liquids must convert to a vapor before they will burn. The characteristic that describes how easily these fuels can be converted to a vapor is the flashpoint. The flashpoint is defined as the temperature at which the fuel produces enough vapors to form an ignitable mixture with air at its surface.

If the temperature of the fuel is below its flashpoint, it cannot produce enough vapors to burn since its evaporation rate is too slow. Whenever a fuel is at or above its flashpoint, vapors are present. The flashpoint is not the temperature at which the fuel bursts into flames; that is the autoignition temperature.

The flashpoint is always lower than the boiling point. For fuels that are gases at atmospheric conditions (like hydrogen, methane and propane), the flashpoint is far below ambient temperature and has little relevance since the fuel is already fully vaporized. For fuels that are liquids at atmospheric conditions (such as gasoline or methanol), the flashpoint acts as a lower flammability temperature limit.

Fuel	Flashpoint
Hydrogen	< –423 ºF (< –253 ºC; 20 K)
Methane	–306 ºF (–188 ºC; 85 K)
Propane	–156 ºF (–104 ºC; 169 K)
Gasoline	Approximately –45 ºF (–43 ºC; 230 K)
Methanol	52 ºF (11 ºC; 284 K)

Table 1-5 Flashpoint of Comparative Fuels

Flammability Range

The flammability range of a gas is defined in terms of its lower flammability limit (LFL) and its upper flammability limit (UFL). The LFL of a gas is the lowest gas concentration that will support a self-propagating flame when mixed with air and ignited. Below the LFL, there is not enough fuel present to support combustion; the fuel/air mixture is too lean.

The UFL of a gas is the highest gas concentration that will support a self-propagating flame when mixed with air and ignited. Above the UFL, there is not enough oxygen present to support combustion; the fuel/air mixture is too rich. Between the two limits is the flammable range in which the gas and air are in the right proportions to burn when ignited.

A stoichiometric mixture occurs when oxygen and hydrogen molecules are present in the exact ratio needed to complete the combustion reaction. If more hydrogen is available than oxygen, the mixture is rich so that some of the fuel will remain unreacted although all of the oxygen will be consumed. If less hydrogen is available than oxygen, the mixture is lean so that all the fuel will be consumed but some oxygen will remain. Practical internal combustion and fuel cell systems typically operate lean since this situation promotes the complete reaction of all available fuel.

One consequence of the UFL is that stored hydrogen (whether gaseous or liquid) is not flammable while stored due to the absence of oxygen in the cylinders. The fuel only becomes flammable in the peripheral areas of a leak where the fuel mixes with the air in sufficient proportions.

Two related concepts are the lower explosive limit (LEL) and the upper explosive limit (UEL). These terms are often used interchangeably with LFL and UFL, although they are not the same. The LEL is the lowest gas concentration that will support an *explosion* when mixed with air, *contained* and ignited. Similarly, the UEL is the highest gas concentration that will support an explosion when mixed with air, contained and ignited.

An explosion is different from a fire in that for an explosion, the combustion must be contained, allowing the pressure and temperature to rise to levels sufficient to violently destroy the containment. For this reason, it is far more dangerous to release hydrogen into an enclosed area (such as a building) than to release it directly outdoors.

Hydrogen is flammable over a very wide range of concentrations in air (4 – 75%) and it is explosive over a wide range of concentrations (15 – 59%) at standard atmospheric temperature. The flammability limits increase with temperature as illustrated in Figure 1-6. As a result, even small leaks of hydrogen have the potential to burn or explode. Leaked hydrogen can concentrate in an enclosed environment, thereby increasing the risk of combustion and explosion. The flammability limits of comparative fuels are illustrated in Figure 1-7.

Mixtures of hydrogen and air are potentially flammable or explosive.

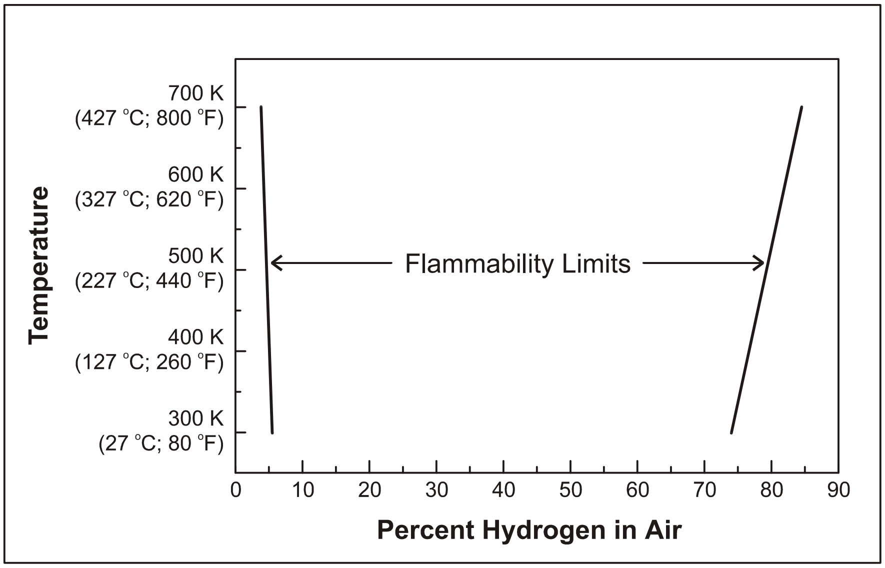


Figure 1-6 Variation of Hydrogen Flammability Limits with Temperature

Key Points & Notes

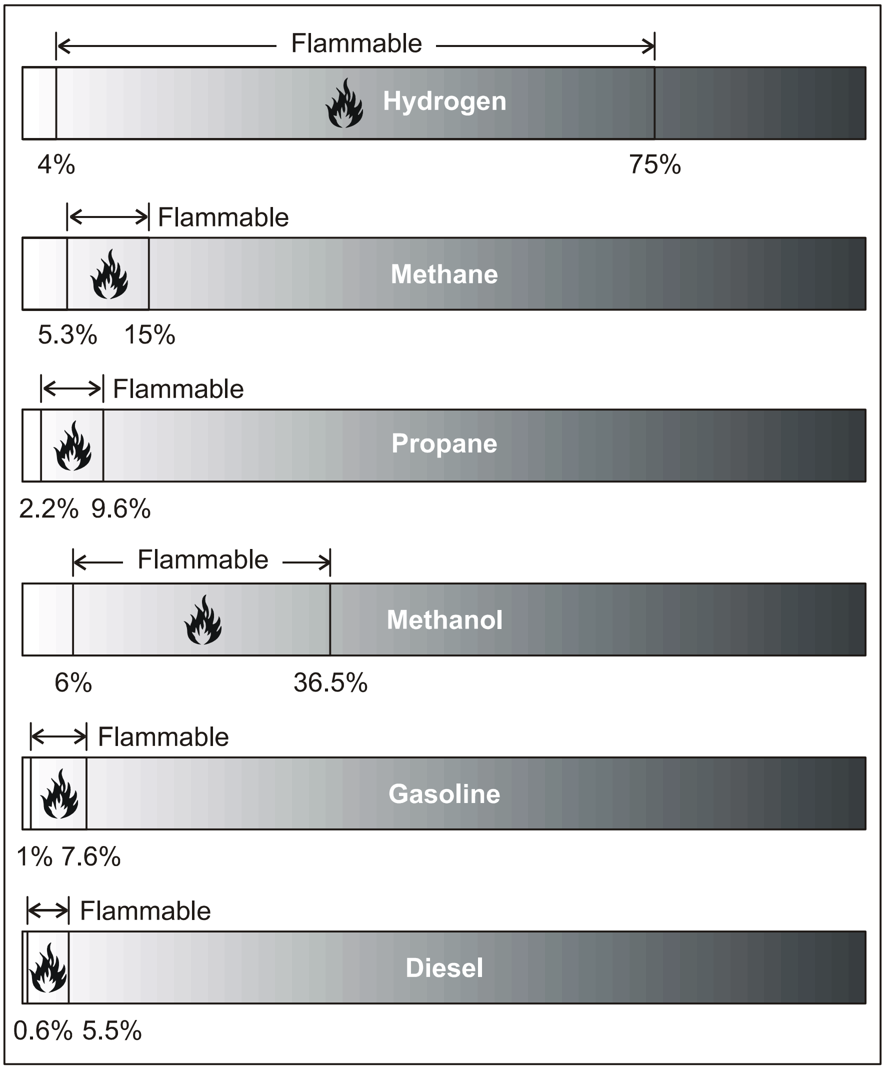


Figure 1-7 Flammability Ranges of Comparative Fuels at Atmospheric Temperature

Autoignition Temperature

The autoignition temperature is the minimum temperature required to initiate self-sustained combustion in a combustible fuel mixture in the absence of a source of ignition. In other words, the fuel is heated until it bursts into flame.

Each fuel has a unique ignition temperature. For hydrogen, the autoignition temperature is relatively high at 1085 °F (585 °C). This makes it difficult to ignite a hydrogen/air mixture on the basis of heat alone without some additional ignition source. The autoignition temperatures of comparative fuels are indicated in Table 1-6.

Key Points & Notes

Fuel	Autoignition Temperature
Hydrogen	1085 ºF (585 ºC)
Methane	1003 ºF (540 ºC)
Propane	914 ºF (490 ºC)
Methanol	725 ºF (385 ºC)
Gasoline	450 to 900 ºF (230 to 480 ºC)

Table 1-6 Autoignition Temperature of Comparative Fuels

Octane Number

The octane number describes the anti-knock properties of a fuel when used in an internal combustion engine. Knock is a secondary detonation that occurs after fuel ignition due to heat buildup in some other part of the combustion chamber. When the local temperature exceeds the autoignition temperature, knock occurs.

The performance of the hydrocarbon octane is used as a standard to measure resistance to knock, and is assigned a relative octane rating of 100. Fuels with an octane number over 100 have more resistance to auto-ignition than octane itself. Hydrogen has a very high research octane number and is therefore resistant to knock even when combusted under very lean conditions. The octane number of comparative fuels are indicated in Table 1-7. The octane number has no specific relevance for use with fuel cells.

Fuel	Octane Number
Hydrogen	130+ (lean burn)
Methane	125
Propane	105
Octane	100
Gasoline	87
Diesel	30

Table 1-7 Octane Numbers of Comparative Fuels

Ignition Energy

Ignition energy is the amount of external energy that must be applied in order to ignite a combustible fuel mixture. Energy from an external source must be higher than the autoignition temperature and be of sufficient duration to heat the fuel vapor to its ignition temperature. Common ignition sources are flames and sparks.

Although hydrogen has a higher autoignition temperature than methane, propane or gasoline, its ignition energy at 1.9 x 10^{-8} Btu (0.02 mJ) is about an order of magnitude lower and is therefore more easily ignitable. Even an invisible spark or static electricity discharge from a human body (in dry conditions) may have enough energy to cause ignition. Nonetheless, it is important to realize that the ignition energy for all of these fuels is very low so that conditions that will ignite one fuel will generally ignite any of the others.

Hydrogen has the added property of low electro-conductivity so that the flow or agitation of hydrogen gas or liquid may generate electrostatic charges that result in sparks. For this reason, all hydrogen conveying equipment must be thoroughly grounded.

Flammable mixtures of hydrogen and air can be easily ignited.

Burning Speed

Burning speed it the speed at which a flame travels through a combustible gas mixture.

Burning speed is different from flame speed. The burning speed indicates the severity of an explosion since high burning velocities have a greater tendency to support the transition from deflagration to detonation in long tunnels or pipes. Flame speed is the sum of burning speed and displacement velocity of the unburned gas mixture.

Burning speed varies with gas concentration and drops off at both ends of the flammability range. Below the LFL and above the UFL the burning speed is zero.

The burning speed of hydrogen at 8.7–10.7 ft/s (2.65–3.25 m/s) is nearly an order of magnitude higher than that of methane or gasoline (at stoichiometric conditions). Thus hydrogen fires burn quickly and, as a result, tend to be relatively short-lived.

Quenching Gap

The quenching gap (or quenching distance) describes the flame extinguishing properties of a fuel when used in an internal combustion engine. Specifically, the quenching gap relates to the distance from the cylinder wall that the flame extinguishes due to heat losses. The quenching gap has no specific relevance for use with fuel cells.

The quenching gap of hydrogen (at 0.025 in; 0.064 cm) is approximately 3 times less than that of other fuels, such as gasoline. Thus, hydrogen flames travel closer to the cylinder wall before they are extinguished making them more difficult to quench than gasoline flames. This smaller quenching distance can also increase the tendency for backfire since the flame from a hydrogen-air mixture can more readily get past a nearly closed intake valve than the flame from a hydrocarbon-air mixture.

Flame Characteristics

Hydrogen flames are very pale blue and are almost invisible in daylight due to the absence of soot. Visibility is enhanced by the presence of moisture or impurities (such as sulfur) in the air. Hydrogen flames are readily visible in the dark or subdued light. A hydrogen fire can be indirectly visible by way of emanating “heat ripples” and thermal radiation, particularly from large fires. In many instances, flames from a hydrogen fire may ignite surrounding materials that do produce smoke and soot during combustion.

Hydrogen flames are almost invisible in daylight.

Figure 1-8 Invisible Hydrogen Flame Igniting Broom

Hydrogen fires can only exist in the region of a leak where pure hydrogen mixes with air at sufficient concentrations. For turbulent leaks, air reaches the centerline of the leakage jet within about five diameters of a leakage hole, and the hydrogen is diluted to nearly the composition of air within roughly 500 to 1000 diameters. This rapid dilution implies that if the turbulent leak were into open air, the flammability

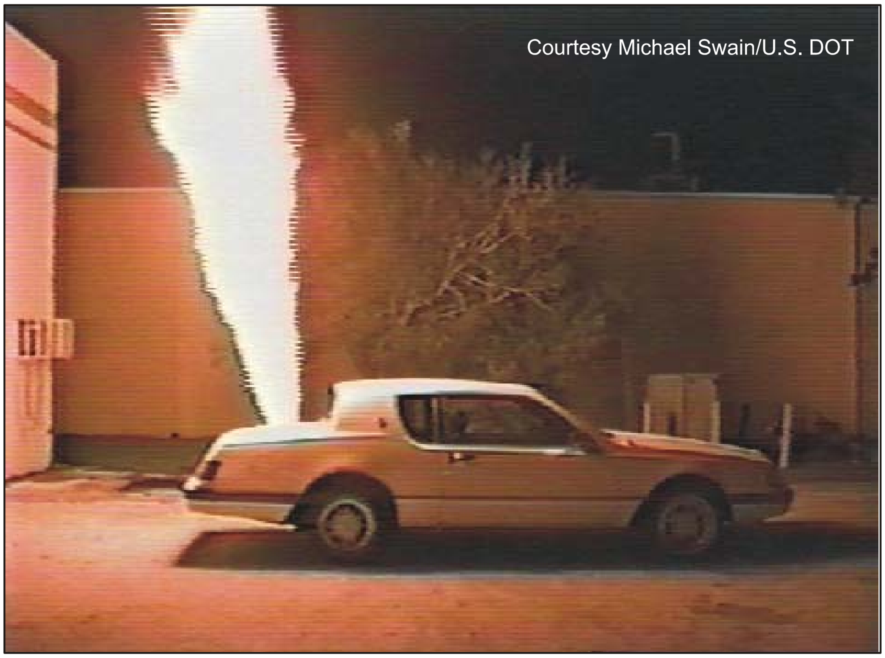
Key Points & Notes

Corn brooms are sometimes used by emergency response personnel to detect hydrogen flames.

zone would exist relatively close to the leak. Therefore, when the jet is ignited, the flame length is less than 500 diameters from the hole (for example, for a 0.039 in/1 mm diameter leak, the flame length will be less than 19.7 in/0.5 m).

In many respects, hydrogen fires are safer than gasoline fires. Hydrogen gas rises quickly due to its high buoyancy and diffusivity. Consequently hydrogen fires are vertical and highly localized. When a car hydrogen cylinder ruptures and is ignited, the fire burns away from the car and the interior typically does not get very hot.

Gasoline forms a pool, spreads laterally, and the vapors form a lingering cloud, so that gasoline fires are broad and encompass a wide area. When a car gasoline tank ruptures and is ignited, the fire engulfs the car within a matter of seconds (not minutes) and causes the temperature of the entire vehicle to rise dramatically. In some instances, the high heat can cause flammable compounds to off-gas from the vehicle upholstery leading to a secondary explosion.



Courtesy Michael Swain/U.S. DOT

Figure 1-9 Hydrogen Flame from Ruptured Fuel Cylinder

Hydrogen burns with greater vigor than gasoline, but for a shorter time. Pools of liquid hydrogen burn very rapidly at 0.098 to 0.197 ft/min (3 to 6 cm/min) compared to 0.0098 to 0.00656 ft/min (0.3 to 1.2 cm/min) for liquid methane, and 0.00656 to 0.0295 ft/min (0.2 to 0.9 cm/min) for gasoline pools.

Hydrogen emits non-toxic combustion products when burned. Gasoline fires generate toxic smoke.

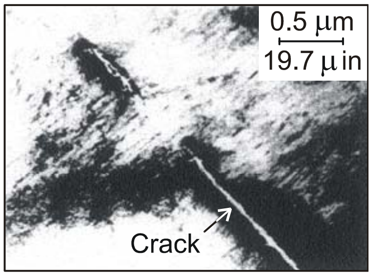
1.3.4 Hydrogen Embrittlement

Constant exposure to hydrogen causes a phenomenon known as hydrogen embrittlement in many materials. Hydrogen embrittlement can lead to leakage or catastrophic failures in metal and non-metallic components.

The mechanisms that cause hydrogen embrittlement effects are not well defined. Factors known to influence the rate and severity of hydrogen embrittlement include hydrogen concentration, hydrogen pressure, temperature, hydrogen purity, type of impurity, stress level, stress rate, metal composition, metal tensile strength, grain size, microstructure and heat treatment history. Moisture content in the hydrogen gas may lead to metal embrittlement through the acceleration of the formation of fatigue cracks.

Materials in contact with hydrogen are subject to hydrogen embrittlement.

Key Points & Notes



Hydrogen Embrittlement

1.4 Gas Laws

Key Points & Notes

Gas laws deal with how gases behave in response to changes in pressure, temperature or volume.

Pressure

Pressure is the exertion of continuous force on or against a body by another in contact with it. Pressure is expressed as force per unit area.

Since pressure is force per area (F/A), and force is mass times acceleration (m•a), pressure can also be understood as mass times acceleration per area (m•a/A). The atmosphere has mass and gravity accelerates this mass towards the earth, so there is atmospheric pressure on every area of earth. Atmospheric pressure is also known as air pressure or barometric pressure.

We do not feel air pressure because it is exerted in all directions, not just downward. It is also acts within our bodies — this serves to balance the pressure outside out bodies so that we do not notice its presence.

Although gravity holds the atmosphere to the earth, it is unable to draw all of the air molecules to the surface of the earth. This is because the forces associated with the gas molecules' movements (as they jostle each other) are much stronger than gravity and resist being drawn together.

All gases are compressible, that is, they can be compressed into a smaller volume with pressure. The pressure of the atmosphere itself causes stratification of the air, with the densest levels near the earth's surface. The density of the atmosphere continues to decrease as we look far above the earth's surface to where the sparse air molecules are no longer different than those in interplanetary space.

Air pressure at sea level is defined as one atmosphere (1 atm), which is about 15 psia or 1 bara or 100 kPa. Air pressure varies with altitude and weather changes. At 7000 ft (2134 m) altitude, the air pressure is only 11.5 psia (0.79 bara). The weight of the air is corresponding less at higher elevations, reducing by about 3% for every 1000 ft (305 m). The lower the pressure, the lower the boiling point of liquids, such that on the top of Mt. Everest, boiling water is little more than tepid. We notice this change in air pressure when out ears pop as we change altitude.

A carbureted internal combustion engine that is finely tuned at sea level, runs lean at a higher altitude.

Pressure greater than air pressure is called positive pressure, while negative pressure is that below air pressure.

Key Points & Notes

Volume

When we study gas within a container — a fixed volume — we find that the gas pressure is still equal in all directions (Pascal's Law). The pressure of a contained gas is the force exerted by its molecules against the walls of the container. The pressure is determined by the number of molecules within the container. The more molecules, the greater the pressure, as more molecules are colliding with the walls.

When we press more gas into a container, we move it from its lower-pressure higher-volume source to the higher-pressure lower-volume container. As we force more gas into the container (such as during fueling), the volume of the gas is reduced, while the pressure is increased.

Pressure also increases when the volume of the container is reduced, such as during the compression stroke of an internal combustion engine.

Boyle's Law: Pressure vs Volume

The relationship between pressure and volume was first shown by Boyle in 1662, who demonstrated that:

> The pressure of a given mass of gas is inversely proportional to its volume at a constant temperature.

Expressed mathematically, Boyle's Law (or the first gas law) is:

$$P_1V_1 = P_2V_2$$

where:

P = absolute pressure
V = volume

Charles' Law: Temperature vs Volume

Whereas Boyle studied pressure, later scientists observed that temperature also had an effect on volume. Charles quantified the temperature change (1787), and his law (the second gas law) states that:

> The volume of an ideal gas at constant pressure is directly proportional to the absolute temperature.

Key Points & Notes

Charles was the first to realize that temperature had to be measured in absolute terms, leading to the definition of absolute zero. Expressed mathematically, Charles' Law (the second gas law) is:

$$\frac{V_1}{V_2} = \frac{T_1}{T_2}$$

where:

T = absolute temperature
V = volume

Whereas Boyle relates pressure (P) to temperature (T), Charles relates pressure (P) to temperature (T). Logically, temperature (T) also relates to pressure (P), as in:

$$\frac{P_1}{P_2} = \frac{T_1}{T_2}$$

Ideal Gas Law: Pressure, Temperature and Volume

The third or ideal gas law combines Boyle's and Charles' laws into the single equation:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

A change in one of the variables (absolute pressure, absolute temperature or volume) must result in a change in one or both of the other variables. The same relationship can be expressed as:

$$PV = n\bar{R}T$$

where:

P = absolute pressure
V = volume
n = number of moles of gas molecules present
T = absolute temperature
$\bar{R}$ = universal gas constant = 3.4067 ft-lb/mol °F (8.31434 Nm/mol K)

A mole is simply a collection of 6.023×10^{23} molecules. This large number turns out to be a convenient unit in chemistry, and the mass of one mole of any pure substance is known with great accuracy. For hydrogen, every mole of hydrogen molecules (H_2) has a mass of 4.445×10^{-3} lb (2.016×10^{-3} kg).

The gas relationship can therefore be written in terms of mass instead of moles *for a specific substance* as:

$$PV = mRT$$

where:

m = mass of gas molecules present
R = specific gas constant. For hydrogen this constant is 766.8 ft-lb/lb °F (4124.18 Nm/kg K)

Furthermore, as density (⑧) is the amount of mass in a given volume (m/V), we can substitute density into the same equation:

$$P = \rho R T$$

This gas relationship was considered accurate into the 20th century, but was finally found to be only an approximation. We now describe the third gas law as the *ideal* gas law as we realize that it only describes an ideal gas, that is, a gas consisting of molecules occupying negligible space and without attraction for each other.

The ideal gas law cannot be applied to liquids.

In reality, gas molecules do occupy space, although very little, and they do attract one another, although very weakly. The space that the molecules occupy slightly reduces the volume available to hold more gas, and the molecules attraction for each other slightly increases the pressure.

The ideal gas relationship can be used accurately to describe the behavior of real gases at pressures up to approximately 1450 psig (100 barg) at normal ambient temperatures. At higher pressures, the results become increasingly inaccurate as illustrated in Figure 1-10.

Hydrogen is commonly stored as a high-pressure gas at up to 3600 or even 5000 psig (250 to 350 barg) at ambient temperatures. Therefore, the ideal gas relationship cannot be used accurately at gas storage pressures.

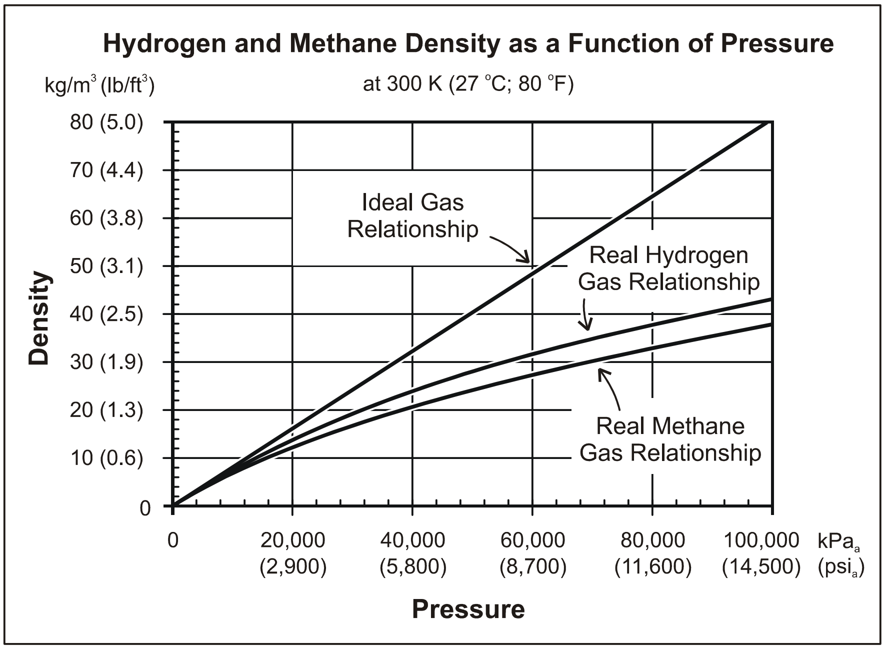


Figure 1-10 Hydrogen Density as a Function of Pressure

Key Points & Notes

The resulting deviation from the ideal gas law is always in the form of compression — the gas occupies less space than the ideal gas law predicts. One of the simplest ways of correcting for this additional compression is through the addition of a compressibility factor, designated by the symbol Z.

Compressibility factors (or "Z factors") are derived from data obtained through experimentation and depend on temperature, pressure and the nature of the gas. The Z factor is then used as a multiplier to adjust the ideal gas law to fit actual gas behavior as follows:

$$P = Z\rho RT$$

Key Points & Notes

1.5 Key Engineering Parameters and Their Measurement

The key parameters with respect to gases are:

- pressure
- temperature
- volume/capacity
- mass and weight
- mass flow

These parameters are measured in engineering units.

1.5.1 Pressure

Pressure can be measured by a variety of instruments, including:

- barometers and altimeters
- pressure gauges
- pressure transducers or transmitters (digital manometers)

Barometers measure atmospheric pressure, originally using mercury in a tube to measure pressure changes. Modern barometers are of aneroid type, consisting of a hermetically sealed metal box, exhausted of air. The top and bottom of the box are made of thin corrugated plates held apart by a spring. The top plate is pressed outwards by the spring and inwards by air pressure. Movement of the top plate with changes in air pressure is transferred to a pointer on a scale. The familiar altimeter is a type of sensitive aneroid barometer.

Pressure gauges are normally designed to read either *gauge* or *absolute* pressure. Gauge pressure is measured *relative to the pressure of the air* at sea level. Thus, gauge measurements of air pressure at sea level are always zero regardless of the units used. Absolute pressure is measured *relative to a perfect vacuum.* Thus, absolute measurements of air pressure at sea level result in a value of 14.7 psig (or equivalent, depending on the units).

Pressure gauges come in various designs. A U-tube manometer is a simple pressure gauge that either has both ends of the tube open to the atmosphere or one end closed in a vacuum over the sealing liquid. A ring balance pressure gauge

Key Points & Notes

is similar to the U-tube type except that the tube is pivotally mounted.

The widely used spring-tube (or Bourdon-tube) pressure gauge measures pressure on the basis of the deformation of an elastic measuring element (i.e. a curved tube). In a diaphragm pressure gauge the elastic element is a stiff metallic diaphragm held between two flanges; pressure is applied to the underside of the diaphragm and the movement of the latter is transmitted to a pointer.

A vacuum gauge is a differential pressure gauge. It measures the difference between atmospheric and less-than-atmospheric pressure.

Pressure transmitters or transducers have the advantage over pressure gauges that they can send an electronic signal to a control system. Pressure transmitters typically consist of a mechanical bellows in contact with the process stream upon which is bonded a strain gauge. As the bellows move due to a change in pressure, the strain gauge registers the motion and converts it to a proportional change in resistance. These pressure-induced resistance changes are too small to be monitored by the control system directly. As a result, a transmitter converts (conditions) the transducer resistance to a high-level analog voltage or current signal and sends this signal to the control system. This analog signal varies with pressure in the same way as the original resistance. Once received, the signal can be converted to engineering units for display on a digital readout device.

Units of Pressure

Pressure can be expressed in any unit that comprises a force divided by an area. Some common units of pressure are:

- pounds per square inch (psi)
- Pascals (Pa), kilopascals (kPa), megapascals (MPa), and gigapascals (GPa)
- bars and millibars (mbar)
- atmospheres (atm)

Pressure is given as either absolute, or relative to atmospheric pressure. The subscript (or postscript) *a* is used to denote absolute pressure, and *g* to denote *gauge* or pressure relative to atmospheric. When using pounds-per-square-inch, the values 15 psia and 0 psig are equivalent, as atmospheric pressure is approximately 15 psia (14.504 psig). Likewise in metric, 1.0 bara equals 0 barg.

Key Points & Notes

Where no subscript is appended, it usually means the value is absolute (as in this manual), although some authors do the opposite and drop the subscript to mean gauge!

Other standard units of pressure are "inches of water" or "inches of mercury". These measures refer to how high a column of water or mercury rises within a tube in response to pressure (at 68 °F; 20° C). Likewise, millimeters or centimeters of mercury are also used to quantify pressure. Each millimeter of mercury is also known as one "torr".

The metric unit Pascal (Pa) is defined as one Newton per square meter (N/m^2). This unit is impractically small for most purposes, so the larger units of kilopascal (kPa = 1000 Pa), megapascal (MPa = 10^6 Pa), and gigapascal (Gpa = 10^9 Pa) are more commonly used.

Refer to Module 11 for additional conversions.

Conversions — Units of Pressure

Unit	Accurately Multiply By	Roughly Multiply By	To Get
Standard to Standard			
psi	0.068 046	0.07	atm
psi	2.04	2	in Hg
Standard to Metric			
psi	6.894 757	7	kPa
psi	0.068 948	0.07	bar
atm	1.013 25	1	bar
Metric to Standard			
kPa	0.145 038	0.15	psi
bar	14.503 77	15	psi
Metric to Metric			
bar	1000		millibar
bar	100		kPa
kPa	1000		Pa
MPa	1000		kPa

1.5.2 Temperature

Temperature is the degree or intensity of heat of a substance in relation to others. This should not be confused with heat, which is a form of energy arising from molecular motion. Heat is energy, whereas temperature is an arbitrary measure of relative heat intensity.

Temperature can be measured by a variety of means, but the most important are:

- thermometers
- temperature transducers (RTD's)
- thermocouples

Thermometers are most familiar to us as a measuring device that uses a column of mercury within a narrow glass tube. As the temperature rises, the mercury expands and rises up the tube. A calibrated temperature scale beside the tube indicates the corresponding temperature. Substances other than mercury are used for temperatures below –40° or for very high temperatures.

A thermometer can be based on any substance that changes in some manner with temperature. A resistance thermometer is based on the variation of electrical resistance with temperature. A bimetallic thermometer in made of two strips of dissimilar metal soldered together, so that the differing reaction to temperature of the two metals causes the soldered mass to lean in one direction or the other. Simple household thermostats use such a bimetal strip. A thermostat combines a thermometer with a switch that closes a circuit, or causes some action, when a temperature setting is reached.

Temperature transducers typically consist of an element that is in contact, directly or indirectly, with a process stream or equipment part. This element changes its resistance in proportion to its temperature and is commonly known as a *resistive temperature device* (RTD). These temperature-induced changes in resistance are too small to be monitored by the control system directly. As a result, a transmitter conditions the resistance to a high-level voltage or current signal and sends this signal to the control system. This analog signal varies with temperature in the same way as the original resistance. Once received, the signal can be converted to engineering units for display on a digital readout device.

Key Points & Notes

Thermocouples also generate a voltage in proportion to temperature. A thermocouple consists of two wires of different metals connected together; a voltage develops at the junction in proportion to the temperature difference. This voltage can be used as an analog input signal to a control system much like an RTD.

Conversions — Units of Temperature

The standard measure of temperature, degrees Fahrenheit (°F), uses 0° as the temperature at which heavily *salted* water freezes, and 100° as approximately human body temperature. On this system, at one atmosphere, pure water freezes at 32° and boils at 212° — a range of 180°.

The metric measure of temperature, degrees Celsius or Centigrade (°C), is based on the freezing and boiling points of pure water at one atmosphere. On this system, water freezes at 0° and boils at 100° — a range of 100°.

Comparing the ranges, each Fahrenheit degree is 100 °C/180 °F or 5/9 of a Celsius degree. To convert specific temperatures, both the range and the zero point for the scales must be converted as follows:

$$°C = (°F - 32) \times 5/9 \qquad °F = °C \times 9/5 + 32$$

A rough conversion is:

$$°C = (°F - 30) \times 1/2 \qquad °F = °C \times 2 + 30$$

The Fahrenheit and Celsius temperature scales give no indication of how much hotter or colder one temperature is from another in an absolute sense. To do this, an *absolute* temperature scale is needed relative to *absolute zero*, the lowest temperature in the universe. All molecular motion stops at absolute zero.

Both the standard and metric systems have absolute scales. In standard, the Rankine system uses the symbol °R for degrees *Fahrenheit* above absolute zero. In metric, the Kelvin system uses the symbol K for degrees *Celsius* above absolute zero. Absolute zero is 0 °R or 0 K. (No degree symbol is used with K.) Since absolute zero is –273.15 °C or –459.67 °F, the conversions within systems are:

$$K = °C + 273.15 \qquad °R = °F + 459.69$$

Both systems of absolute temperature use absolute zero as the zero point of their scales, so only the ranges need be converted between standard and metric:

$$K = °R \times 5/9 \qquad °R = K \times 9/5$$

1.5.3 Volume and Capacity

Key Points & Notes

Volume is 3-dimensional space. Capacity (or “water capacity”) is the volume contained within a vessel.

As volume is 3-dimensional, it is represented by a cubed measure of length, such as cubic inches (in^3), cubic feet (ft^3), cubic miles (mi^3), cubic millimeters (mm^3), cubic centimeters (cm^3 or cc), cubic meters (m^3), etc. Any linear measure can be cubed to become a volumetric measure. Cubic measures cannot be a combination of different measures, such as $ft\text{-}in^2$.

Capacity or liquid measure expresses the volume of a vessel. Standard capacity measures include fluid ounces (fl oz), cups (c), pints (pt), quarts (qt), and gallons (gal).

Imperial liquid measures used in Britain, Canada, Australia and other Commonwealth countries have fluid ounces that are 4% larger than in standard; and pints, quarts and gallons that contain 5/4 as many fluid ounces as the standard measures of the same name. When referring to published specifications, and the type of liquid measure is not given, check the country of publication.

Metric measure of capacity centers around liters (L), and the correspondingly smaller milliliters (mL). In metric, volumetric measurements are directly linked to liquid measures. The relationship is expressed as:

$$1\ cm^3 = 1\ mL \qquad 1000\ cm^3\ (1\ dm^3) = 1\ L \qquad 1\ m^3 = 1000\ kL$$

In standard units, there is no such intuitively convenient relationship between volumetric and liquid measures. Rather:

$$1\ in^3 = 0.6\ fl\ oz \qquad 1\ ft^3 = 7.5\ gal$$

$$1\ fl\ oz = 1.8\ in^3 \qquad 1\ gal = 0.13\ ft^3$$

Conversions — Units of Volume and Capacity

Unit	Accurately Multiply By	Roughly Multiply By	To Get
Standard to Standard			
ft^3 *or* cu ft (cubic feet)	1728	1700	in^3 *or* cu in (cubic inches)
ft^3	7.480519	7.5	gal
gal	0.133 681	0.13	ft^3
in^3	0.554	0.6	fl oz
fl oz (US fluid ounce)	1.804 688	2	in^3
gal (US gallon)	4		qt (quarts)
gal	128	130	fl oz
Standard to Metric			
in^3	16.387 064	16	cm^3 (cubic centimeter) or mL (milliliter)
ft^3	28.316 85	30	L (liter)
ft^3	0.028 317	0.03	m^3 (cubic meter) or kL (kiloliter)
fl oz	29.573 53	30	cm^3 or mL
gal	3.785 412	4	L
Metric to Standard			
cm^3 or mL	0.061 024	0.06	in^3
cm^3 or mL	0.033 813	0.03	fl oz
m^3 or kL	35.314 475	35	ft^3
Metric to Metric			
cm^3 or mL	1000		mm^3
L	1000		cm^3
m^3 or kL	1000		L

Key Points & Notes

Refer to Module 11 for additional conversions.

1.5.4 Mass and Weight

Key Points & Notes

Mass and weight are not the same thing. Mass is the amount of matter that a body contains. Weight is a force, and a force is equal to mass times acceleration ($F = ma$). Thus, when a body experiences the acceleration of the earth's gravity, it exerts a force on the surface of the earth which is weight. A body in outer space does not experience weight, but it has mass.

The standard unit for both mass and weight is the pound (lb) which adds to the general confusion. Strictly speaking, a pound-mass (sometimes written lb_m) is the amount of mass that results in one pound of force under the influence of the earth's gravity. A pound-force (sometimes written lb_f) is a force of one pound, pure and simple.

The metric unit for mass is the kilogram (kg) and the unit for force, and therefore weight, is the Newton (N or $kg\text{-}m/s^2$). Unfortunately, people tend to think of kilograms as weight thereby instilling the same confusion that surrounds the use of the unit pound. A "weight" of one kilogram is really the force exerted under the influence of the earth's gravity which is 9.8 N.

As the earth is not a sphere but an oblate spheroid (it bulges at the equator) the earth's gravity is not constant. This results in reduced gravity at the bulge or at higher elevations. An object that weighs 200 lb at the North Pole, also weighs 200 lb at the South Pole, but only 199 lb at the equator. The mass of the object, however, remains the same.

Spelling differentiates the standard ton and the metric tonne. The tonne of 1000 kg (2200 lb) is only 10% larger than the short ton of 2000 lb, and virtually the same as the long ton of 2240 lb.

In metric, the relationship between volume and capacity is extended to include mass in kilograms (kg) in the special case of water at one atmosphere and 4 °C. Specifically:

1000 cm^3 or 1 L of water has the mass of 1 kg

Likewise, a milliliter has a mass of one gram, and a cubic meter of water has a mass of one tonne. This relationship makes it particularly easy to convert between the volume, capacity and mass of water. The 4 °C is used as water is at its maximum density at that temperature — water has the rare property that it expands through both cooling and heating.

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To state the equivalent in standard units, also with fresh water at its maximum density (39 °F):

One cubic foot or 7.5 gallons of water weighs 62.5 pounds.

One gallon or 0.134 ft^3 *of water weighs 8.35 pounds.*

Conversions —Units of Mass

Unit	Accurately Multiply By	Roughly Multiply By	To Get
Standard to Standard			
lb (pound)	16		oz (ounce)
ton — short	2000		lb
Standard to Metric			
oz	28.350	30	g (gram)
lb	0.453 59	0.5	kg (kilogram)
ton — short	0.907 18	0.9	tonne
Metric to Standard			
g	0.035 273	0.035	oz
kg	2.204 586	2.2	lb
tonne	1.102 293	1.1	ton — short
Metric to Metric			
g	1000		mg
kg	1000		g
tonne	1000		kg

Refer to Module 11 for additional conversions.

1.5.5 Mass Flow

Gas flow is the motion of a gas from a higher pressure zone to a lower pressure zone. There is resistance to flow just as there is resistance to electricity passing through a wire. As the gas molecules pass through a pipe, some lose a certain amount of their energy due to friction against the sides of the pipe. Molecules against the sides the pipe move very slowly compared to those in the center.

Gas flow is typically measured using a rotameter or a mass flow meter.

A rotameter consists of one or more balls within a tube. The tube has a scale marked on the outside. As gas flows through the tube, the ball lifts indicating the amount of flow relative to the scale. Rotameters must be chosen to match

Key Points & Notes

the expected flow range and calibrated relative to a specific gas composition, temperature and pressure.

A mass flow meter accurately measures gas flow without requiring compensations for variations in pressure and temperature. The mass flow meter consists of a sensor, a shunt assembly and electronic circuitry. Gas flowing through the mass flow meter passes either through the sensor or the shunt assembly. These two gas flows are proportional to each other so that when the sensor flow is measured, the shunt assembly flow can be determined. The size of the opening in the shunt assembly limits the maximum amount of gas that can flow through the mass flow meter. This flow range, as sensed by the sensor, is converted by the electronic circuitry into a linear output voltage or current signal.

Units of Gas Flow

Common standard units of volumetric fluid flow (fluids include liquids and gases) are cubic feet per minute (ft^3/min), and gallons per minute (gpm). In metric, volumetric flow is typically measured in liters per minute (Lpm).

Volumetric flow can be converted to mass flow by multiplying the volumetric flow by the density of the fluid. This yields standard units such as pounds per second (lb/s) and metric units such as kilograms per second (kg/s).

Liquid densities do not vary appreciably with temperature or pressure since liquids are essentially incompressible. However, gas densities vary significantly with both temperature and pressure as summarized by the ideal gas law. Thus, gas flow measurements must be stated relative to some standard temperature and pressure. A temperature of 0 °C (273 K) and a pressure of 1 atmosphere are used for this purpose.

Using the ideal gas law:

$$V_{STD} = V_M \times \frac{P_M}{P_{STD}} \times \frac{T_{STD}}{T_M} = V_M \times \frac{P_M}{1\ atm} \times \frac{273\ K}{T_M}$$

where:

V_{STD} = standard volume or volumetric flow rate
V_M = measured volume or volumetric flow rate
P_M = absolute measured pressure
P_{STD} = absolute standard pressure (1 atm)
T_M = absolute measured temperature
T_{STD} = absolute standard temperature (273 K)

Consistent units must be used throughout.

Gas volumes corrected in this way use units with the prefix "s", for "standard"; thus, slpm (standard liters per minute) or sft^3/min (standard cubic feet per minute).

Conversions — Gas Mass Flow

Unit	Accurately Multiply By	Roughly Multiply By	To Get
Standard to Standard			
cfm (ft^3/min)	60		cfs (ft^3/s)
cfh (ft^3/hr)	24		cfm (ft^3/min)
gps (gallons per second)	60		gpm
gpm (gallons per minute)	8.020 833	8	cfh (ft^3/hr)
Standard to Metric			
cfm	28.316 85	30	Lpm
cfm	0.028 317	0.03	m^3/min
gpm	3.785 412	3.8	Lpm
Metric to Standard			
Lpm	0.035 315	0.035	cfm (ft^3/min)
Metric to Metric			
m^3/min	1000		Lpm

Key Points & Notes

Refer to Module 11 for additional conversions.