BLEVE: CAUSE & EFFECTS

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Crescent City, Illinois propane explosion occurred in June of 1972 when a freight train with numerous propane cars derailed in the town. The resulting explosion leveled approximately half the town. The water tower in the foreground was over 100 feet tall

BLEVE – CAUSES AND EFFECTS

In the past, there have been many deaths and injuries to firefighting personnel as a result of transportation accidents that led to BLEVES of liquefied flammable gases. Fire Departments normally are the first public agency to be notified when such accidents occur, and accept the responsibility for taking the actions necessary to minimize injury and loss of life and property.

The incidents described in this presentation involve liquefied flammable gases and railroad car containers. BLEVES have occurred in trucks and in fixed tanks containing flammable liquids or gases and the explosions or fire behavior have been similar.

The objectives of this training session are: (1) to define a BLEVE, (2) explain how it occurs, (3) its effect, and (4) methods of prevention. A number of key points need to be discussed, and these should help you to understand the mechanism of these incidents and their possible effects. A good understanding is necessary so that you can make intelligent decisions to minimize the hazard to life and property.

BLEVES can occur in containers of liquids or liquefied gases when a portion of a container is subjected to localized heating. A mechanical BLEVE of containers of liquefied gases can also occur without fire temperature. That is, if the metal is struck by an object or otherwise fails because of mechanical damage. BLEVES are usually extremely violent and produce severe damaging effects.

Remember, a BLEVE is a Boiling Liquid Expanding Vapor Explosion. This potential is always present where mobile or stationary closed containers, tanks and drums are damaged or exposed to fire. The basic explosion is a physical process involving the fracturing of the container, the liquid to vapor transformation and expansion, propulsion of pieces, and shock wave. The chemical properties of the material in the container, for example, flammable or non-flammable, are not factors in the explosion. However, they are of obvious importance in the effects of the explosion.

Fire-caused BLEVES often occur after short periods of fire exposure. The most critical time can be expanded during fire company response and initial layouts. Most fire officers will have little reliable information of how long a tank has been exposed to fire, prior to arrival of fire companies. When you arrive at a flammable liquid or a liquefied flammable gas incident, you must realize that a violent explosion might occur at any moment if the hazardous conditions exist. There is no significant safe period. If the container shell is impinged by fire, or has other wise weakened, the risk of BLEVES will continue until all contents under pressure have been burned or removed. Therefore, the most important situation control decisions must be made almost instantly.

Severe heating by direct flame impingement on the tank(s) above the liquid level is the most critical hazard. Exposure heating, other than direct flame contact, will not lead to a BLEVE unless the contents are firmly unstable or reactive. A combination of both forms of heating can occur. If the flame impingement is on the container shell below the liquid level, much of the heat is absorbed by the liquid. And even though this will increase interior pressure as the heated liquid vaporizes, the tank metal is unlikely to fail at this point. The excess pressure should be relieved by the safety valve. So when you first size up, watch for flame impingement on the tank metal. Try to see if it is above or below the liquid level, remembering that all containers have a vapor space.

Mechanical damage may also have occurred to weaken the tank. Over pressure relief devices may be jammed or otherwise rendered ineffective. Look for this kind of damage. Remember much depends on the amount of pressure that exists inside the tank.

Leaking gas and vapors can ignite from heat sources which are not obvious. Gas or vapors which are heavier than air, and most are, will flow to the lowest level. You will need special gas detectors to identify the pattern of some gas concentrations.

Leakage of gas and vapor, visible and invisible, with or without odor, can form an explosive mixture with air at unpredictable distances, depending on the terrain, the nature of the product involved, and the weather conditions. Although the percentage of gas and air mixture required for an explosion varies with the kind of gas, this is of little significance in outdoor situations, such as we are discussing.

While a BLEVE can occur with water, and does in boilers and water heaters, a BLEVE in which hazardous materials are involved is a far more serious problem. If a tank car or tank truck contains a liquefied flammable gas, such as propane, burning of the material released by the explosion introduces a damaging effect that can the be dominant effect of the entire BLEVE incident. If the material is highly toxic, for example chlorine or anhydrous ammonia, this effect of the released material can be the dominating effect of the BLEVE.

LP gas is transported in liquid form in vehicles, railroad tank cars, and ships. Under normal atmospheric pressure it is a gas, but for economy of movement and storage it is liquefied, reducing its volume. For example, propane when changed from a gas to a liquid, has its volume reduced to $1/270^{th}$ of its gaseous volume. To keep propane as a liquid, pressure must be maintained, requiring tanks of greater strength than those used for gasoline.

Above the liquid level, a vapor space is always left to allow for liquid expansion, as a result of heating from air temperature and sunlight. This is the area of the tank shell that is susceptible to flame impingement damage. You cannot determine the liquid level merely by observation.

At the top of all tanks containing flammable liquids and gases, are devices designed to limit internal pressure. On tank cars these are spring-loaded relief valves in the domes, which also house fittings used for product transfer operations.

On tank trucks, similar relief devices are also located on top, but loading and unloading is most often accomplished from below.

Standards for tank design, marking and placarding, and for the transportation of hazardous materials, are regulated by state and federal agencies.

In a collision or derailment, liquefied gases can be released and vaporized immediately. These vapors can spread over great distances. Because LP gas vapors are heavier than air, they tend to remain close to the ground. The vapors from flammable liquids are also heavier than air.

A spark or other source of ignition can ignite these vapors, causing a flash back to the leaking liquid.

The liquid inside the tank is then heated, boils, and expands, increasing the temperature within the tank. The relief valve may operate to limit the excess pressure. The tank can withstand this pressure only as long as the tank metal retains its design strength.

If the relief valve continues to release pressurized vapor, the liquid level drops, exposing an increasing area of metal to overheating.

Propane in a container at any temperature above its normal boiling point at -44° F, contains heat stored within itself sufficient to vaporize a large portion of the liquid if the pressure is reduced to atmospheric. At 70° F, enough heat exists in the propane liquid to vaporize almost instantly about 1/3 of the liquid propane, if the pressure is reduced to atmospheric pressure.

Vaporization would produce about 270 gallons of propane vapor from each liquid gallon. Can you visualize the resulting vapor cloud from 30,000 gallons?

Heat absorbed by the contained metal in contact with the contained liquid is transferred to the liquid. This is similar to the action of water boiling in an aluminum saucepan. That portion of the contained metal in contact with liquid is unlikely to be in any danger of failure from overheating.

But heat absorbed by the container metal in contact with vapor is retained by the metal, which will begin to approach its melting temperature or other point of failure. This is similar to what happens when water boils or vaporizes in an aluminum saucepan.

Flames contacting the tank above the liquid level create temperatures within the metal high enough to weaken it. When this happens, despite the operation of the relief device, the pressure within the tank can cause the metal to thin and eventually tear.

In most fire-caused BLEVES, involving propane containers, for example, the failure originates in the metal of the vapor space and is characterized by the metal stretching and thinning out and beginning to tear longitudinally.

The longitudinal tear continues, and then starts to become circumferential.

The tanks rips apart. The pressure drops suddenly. Large quantities of boiling liquid vaporize, expand, and ignite immediately. Tank pieces become flying missiles.

Usually a cylindrical tank piece closed at one end will rocket in the direction of its longitudinal axis, but it may be deflected and change direction.

Sections of large tanks can rocket as far as 3500 feet from the original point with devastating velocity trailing flame and even some unburned liquid. However, 1000 to 2000 feet is more common.

In a wreckage, different tanks may be dispersed in alignment and rocket in different directions. On take off or because of the manner in which a crack propagates, the tank may pivot and move in a direction from its original alignment.

Firefighters and bystanders have been killed or dismembered by missile effects.

A ground flash occurs as the mass of burning, expanding vapor is partially confined and channeled by the ground. Personnel in this area are liable to receive massive burns. The ground flash can cover an area hundreds of feet in diameter.

The blast wave or over-pressure can cause glass to shatter and structures to weaken and collapse. Although probably not the greatest threat to firefighters, the effects are serious enough to cause injuries. The blast wave is strong enough to break windows several miles away.

The mass of burning expanding vapor, including that portion in the ground flash, forms a fireball as it rises from the ground. It produces radiant heat sufficient to ignite most combustibles and cause severe flash burns up to 1000 feet beyond the fireball.

The fireball rises on a thermal column radiating heat in all directions.

When faced with a situation in which a BLEVE might occur, the fire officer in command must consider a number of decisions. Any of which could lead to success or failure in controlling the situation. At such a time, the officer's most important need is information. What exactly is the situation? What products are involved? Is it flammable liquid or flammable liquefied gas in the tank? Is there tank damage? Is the relief valve damaged or blocked? Are people in danger? What is the greatest source of water? How much time do we have to take action? If the officer knows the answer to these and similar questions, the decision-making is easy. But chances are that such information is not readily available.

Present and proposed marking and identification systems for containers of flammable liquids and gases make it extremely difficult for fire officers to determine what products are involved, so that their hazard properties can be identified.

The hazardous materials regulations of the D.O.T. require placards to be placed on trucks, trailers, and railroad cars that carry dangerous materials. Vehicles must be placarded on the front, rear, and both sides with the hazard name in letters at least four inches tall. Railroad equipment must be placarded on both sides and ends. Placarding is not required for air shipments. But placards can become detached, destroyed, damaged, or obscured by debris, smoke, or flame.

Train crews or truck drivers may be injured or have left the scene of the accident. Waybills or manifest listing cargo content may be burned or missing. Locating persons who have survived may be difficult. They are not required to make identity known to fire personnel.

Different products may be involved with their own particular hazards. A product may be toxic or explode violently, for reasons other than a BLEVE. It may also be flammable, corrosive, or with mixed dangerous potential. Entering the danger zone to attempt positive identification of the product will entail considerable risk.

The fire officer in command must make a decision on whether to attempt identifying the products if information is not immediately available. If such attempts are deemed necessary, only a minimum number of personnel should be exposed to risks. Every precaution such as full protective clothing, and protective hose lines must be used to provide the highest degree of protection for those entering the danger area.

Extreme care must be used in identifying the correct spelling of the product or products involved. There are many chemicals with similar names, but very different properties, such as hydrochloric acid, or hydrofluoric acid, ammonium nitrate or ammonium nitrite. A mistake in identification could be disastrous. To verify identification write the chemical name of each product, the trade name, manufacturer, carrier, label color and any other symbols. Transmit this immediately to fire alarm headquarters for checking.

If a decision is made to attack the fire, water in large quantities must be applied at the point of flame contact on the tank and to diminish heat of exposure. Tank vapor spaces are the most critical and high priority areas for cooling. But know the capabilities and limitations of hose streams.

500 gallons per minute at each point of flame contact is the minimum water application required for effectiveness in situations when flame is impinging on such tanks. The water source must be capable of sustaining this flow indefinitely. If a film of water exists on the tank shell where it is exposed to flame impingement, the shell cannot become heated to more than 212° F (100° C), a safe temperature.

If a decision is made to approach the fire, only personnel essential to the operations should be put at risk. A fire officer should lead the approach.

Personnel must be given clear instructions on the tactics to be employed and the entire operation must be highly coordinated. The officer should use verbal and hand signals, which have previously been rehearsed and agreed upon by all participants.

Any attempt to extinguish fire by shutting valves or plugging holes, would be tried only after effective cooling streams are striking on the tank shell at points of flame contact. This is a dangerous operation and should be carried out only when absolutely necessary. It is the kind of action that requires realistic practice and training.

Protective clothing currently available provides only minimal protection against flash or heat radiation, and no protection against container fragments. It has, however, saved a number of firefighters from thermal effects of a BLEVE. Wear full protective equipment, including SCBA.

Use of unmanned monitors reduces risk to personnel but the period during set up is often critical in terms of BLEVE potential. The fire officer in command must make a careful estimate of the risks before endangering personnel in this task.

Personnel safety must be considered at all times. The following points should be kept in mind. (1) Approach the fire from the sides of the container. Consider that the tank ends are most dangerous within 60° of the longitudinal axis. (2) Provide wide-angle water spray protection for personnel during initial set up. Be sure to consider the distance range of hose streams. (3) Use all available barriers to protect against flying missiles and thermal radiation. (4) Use unmanned equipment where possible. (5) Maintain observation of areas of flame contact and ensure that water application rates are adequate.

Getting persons out of the zone of immediate risk may require considerable time and personnel. Especially in built up areas. It might even be impossible under some circumstances.

The NFPA strongly recommends that the possibility of BLEVE be considered at all phases of a flammable liquid and a liquefied flammable gas emergency, including the termination phase when the product is being transferred or damaged containers are being moved. Leakage during transfer can result in fire explosion. Containers, especially of liquefied gases, can be damaged severely enough so that a small rise in pressure or movement can result in container failure.

The possibility of BLEVE would dictate that a minimum number of personnel should be exposed to container rupture and that hose lines should be ready for use. Additionally, the possibility of a BLEVE during any phase should be strongly considered when determining whether evacuation property adjacent to the accident should be reoccupied before the problem is totally terminated.

Under the most favorable conditions, this type of incident presents serious danger and threats to the firefighter. The threats also affect the public nearby and this aspect may well have an important bearing on final decisions on commitment of personnel.

If no persons or property are in the danger area, the decision should be relatively simple, and no fire attack should be made.

If only property is at risk, then be very careful about endangering fire personnel in control efforts.

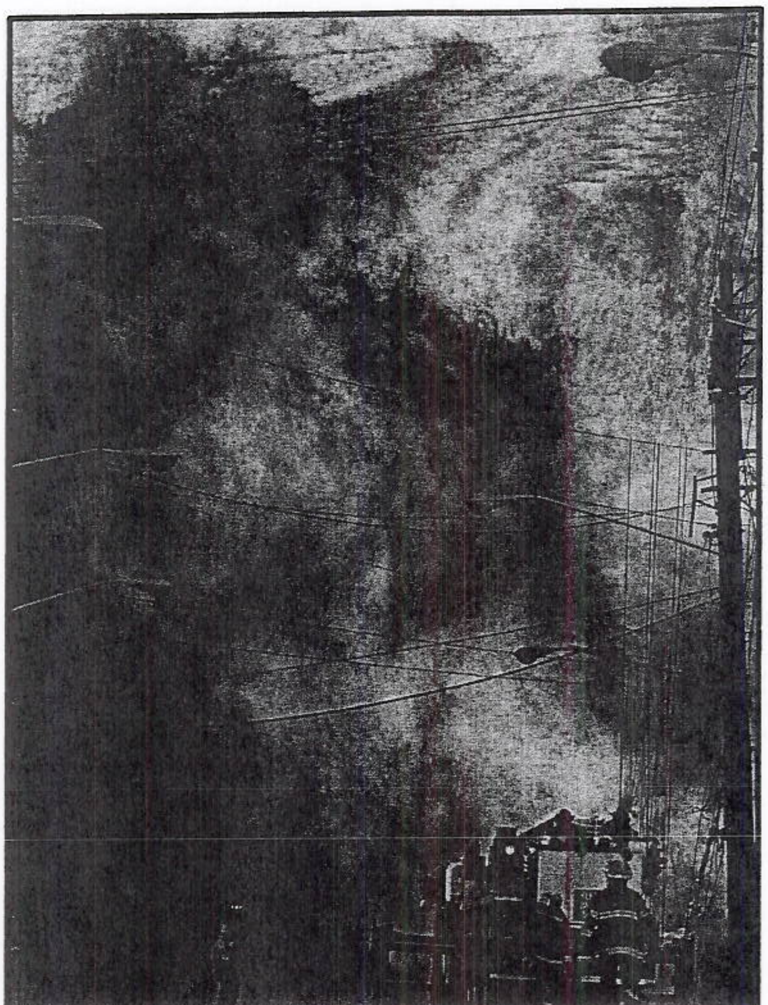
The more difficult decision will be needed when there are occupied premises in the danger area. The fire officer will have to decide whether to start an attack that might control the fire in time to concentrate on removing exposed persons.

Unless the attack is effective, the officer in command will achieve very little, but the choices are influenced by contingencies in each incident. Life safety of the public and firefighters will be the principal consideration.

WHEN TO ANTICIPATE BLEVE

- Activation of PRV
- Sounds from PRV increase
- Pitch from PRV becomes higher and louder
- Space between flame and PRV increases
- Water turns to steam hitting tank

HAZARDS OF GASES



Hazards of Gases

Each and every day of the year, billions of cubic feet of gas are stored, transported, and used without any problems or mishaps. This is the result of a strong conscientious effort toward safety within the gas industry. Even with this effort, from time to time, something goes wrong, either mechanical or human error occurs. When this happens, a hazard to man and his environment may evolve. Because of the laws of nature and of the properties of the gas involved, this hazard can be analyzed and mapped out.

This presentation will analyze these hazards and outline some action that can be taken to nullify, reduce or prevent the hazard from becoming a disaster.

To begin with, there are two fundamental hazards: (1) the hazard of the gas inside of the container, and (2) the hazard of the gas outside of the container.

Should something happen and the gas escape, we would now have a hazard outside of the container which can be divided into either a fire or no fire situation.

If, upon escaping, the gas ignites, we will have a fire condition. Our main concern will be with a heat exposure to people or property. The main objective is to prevent the exposure from being destroyed by the fire.

The best way to accomplish this is to eliminate the heat source. The only way an escaping gas fire should be extinguished is by stopping the flow of gas. The only exception to this rule is to effect an immediate rescue or to facilitate the immediate shutting off of gas. If the gas cannot be shut off, application of water on the exposure, in large quantities, will have to be continued until all of the gas has burned out. The size of the line and the amount of water will vary depending on the size and scope of the fire, but remember you will need to establish a constant water supply. It also will probably have to be in operation for an extended period of time. It is also better to apply water at a rate (GPM) greater than necessary, than to apply not enough. We will expand more on the specifics of fire conditions in a moment, but first let's look at an outside of the container gas hazard under a no fire condition. There are four distinct areas of concern to us of which one or more could apply, depending on what gas is leaking. First, we could have a cryogenic hazard.

The main hazard here is the extreme cold temperature of the liquid. Remember, **"NO LIQUID CAN EXIST AT ATMOSPHERIC PRESSURE, AT A TEMPERATURE ABOVE ITS BOILING POINT."** If there is liquid outside of its container, the temperature of the liquid will be at its boiling point.

The boiling points of some common cryogenic gases are:

Air	-317.8° F	Methane (natural gas)	-258.7° F
Argon	-302.6° F	Nitrogen	-320.4° F
Helium	-452.1° F	Oxygen	-297.4° F
Hydrogen	-423° F		

The boiling point of some other gases not considered cryogenic, but having similar cold hazards are:

Acetylene	-118° F	Methyl chloride	-11° F
Anhydrous ammonia	-28° F	Methyl ether	-11° F
Carbon oxysulfide	-58° F	Propane	-44° F
Cyclopropane	-29° F	Propylene	-53° F
Hydrogen sulfide	-76° F	Propyne (mapp gas)	-10° F
Isobutane	+11° F		

At these cold temperatures anything that comes in contact with the liquid will immediately be frozen. Even the cold vapors close to the liquid could present a cold hazard. You must allow no one to come in contact with any liquid that has a boiling point below the freezing point of water (32° F) as living tissue is largely composed of water and will freeze.

Also, do not let anyone come in contact with any equipment that is displaying a frosting condition, such as piping or valving, as the temperature of these will be close to the same as the liquid it contains.

If someone should come in contact they must seek immediate medical attention.

The second area of concern is the application of water and extinguishing agents on cryogenics.

Remember, the temperature of any liquid gas outside of its container will be below the freezing point of water. Water from a municipal system is generally at a temperature of about 50° F to 70° F, so any application of water will cause an immediate BTU or heat input into the gas liquid. This will cause an immediate increase in the rate of vaporization.

Again, it becomes very important to identify the liquid and to take some facts into consideration.

1. Is it even necessary to apply water?
2. Is the spill in an isolated area where it will cause no problems of any kind if just left to dissipate by itself?

3. Is the spill in an area where applying water will increase the vaporization rate to a dangerous level?
4. Application of high expansion foam will insulate the liquid from the air and slow down the rate of vaporization.

The next area of concern is the asphyxiant hazard where again identification of the product becomes important. Asphyxiant by definition means: "to cause or undergo unconsciousness or death from lack of oxygen."

Remember, man needs oxygen to survive.

The safeguard against this hazard is SCBA. The elimination of this hazard is proper ventilation. You would also have to identify whether the gas is lighter or heavier than air in order to properly ventilate.

The third area of concern is whether the gas in question is combustible or non-combustible. Again, identification of the gas is very important as a leak with no fire could result in either a flammable or a non-flammable gas. The dot marking for flammable gases is a red and white diamond with the four-digit United Nations identification number. There will be a number 2 in the diamond which is the international numerical marking for gases. Do not get this mixed up with the NFPA 704 marking system as flammable gases would have a number 4 in the red or top section. The D.O.T. marking for flammable gases is a red and white colored, diamond shaped placard. The U.N. Identification number will be in the center of the placard. The hazard class number 2 will be located in the bottom tip of the placard.

If the gas is non-flammable, there is no combustion hazard except for oxygen which is a non-flammable gas. As the concentration of oxygen increases above 21%, the ignition temperature of many combustibles is lowered. Also, things burn with much more intensity in oxygen enriched atmospheres. Some examples of non-flammable gases are carbon dioxide, argon, nitrogen, etc.

With the flammable gases such as methane, ethane, propane, butane, acetylene, carbon monoxide and others, the combustion explosion problem is a very major concern. Any time there is a flammable gas exposed to the atmosphere where it can become mixed with oxygen, there is the potential for a combustion explosion. All that is needed is for it to reach a source of heat that is at or above the ignition temperature of the gas.

The combustion explosion hazard can be further broken into two concerns. One being the explosion occurring inside of a structure, the other being the explosion occurring outside of a structure.

Remember, if you extinguish the fire and do not, or are not, able to stop the flow of gas it may eventually reach the same or another source of ignition and ignite again, in which case you will have the same or worse situation.

If the combustion explosion occurs inside of a building, much will depend on how much gas had accumulated prior to ignition. The more gas, the more disastrous the results; in fact, buildings have been leveled and civilians and firefighters killed.

The objective is to prevent the combustion explosion from occurring which, in most cases, is easier said than done. Some methods you may employ are stopping the gas flow, removing sources of ignition or using fog streams to dilute or divert the gas from reaching known ignition sources.

Whenever you are investigating an odor of gas, an industrial gas incident, or an accident involving gas cylinders or tanks, a combustible gas indicator should be used to determine if there is actually a leak, especially where odorless gases are involved, and to determine if the level of concentration has reached the lower flammable limit.

A combustible gas indicator is the only true way to tell.

If you are sending firefighters into buildings to investigate gas leaks and incidents or ventilate a gas leak, without first using a CGI you are asking for a disaster.

Always remember to prepare for the worst and hope for the best. Preparation is the key to success.

The fourth area of concern of a no fire outside container hazard is the toxic hazard.

Once again it becomes vitally important to identify what gas is escaping. Non-toxic gases such as CO_2, Argon, Nitrogen, Methane, and Propane present no physiological or toxic hazard to health. However, such toxic gases as Carbon Monoxide, Acrolein, Ammonia, Chlorine, Phosgene and others can be deadly when inhaling even small amounts.

Some of these gases are flammable and inhaling the smoke from them can be just as deadly.

As a safety procedure SCBA and full protective clothing must be worn, and in some cases, as with ammonia, special clothing must be worn as some toxic gases can be absorbed directly through the skin.

You should keep all personnel out of the area unless it is absolutely necessary for them to be there, and then use only the personnel necessary and no more. You must see that those persons are properly protected.

The old adage, "Do something even if it's wrong" would kill you or your firefighters. You must know what you are dealing with, the potential hazard, and how to alter the course of events that are causing the hazard.

Let us now move to the inside container hazard.

Under normal condition the only hazard is the gases attempt to escape. The major hazard is going to be from an exposure fire. The fire may involve combustibles around the gas containers such as a building, grass, woods, vehicles, etc.

This exposure fire is causing the container and its contents, either liquid or vapor, to be heated and according to Charles' Law, (see Basic and Combined Gas Laws section), raising the gas temperature causes the gas to expand and the pressure to rise. If the pressure rises beyond the design strength of the container, the container will fail.

One thing we must make clear is that strict precautions have to be taken to ensure that oxygen is never mixed with a flammable gas in its container. Therefore, we can never have a fire inside of a container.

The surest method of eliminating the hazard is to extinguish the fire. Extinguishing the fire may not be possible or even advisable as would be the case if the exposing fire were from escaping gas. Then you must treat the tank or container as an exposure and deluge it with water to keep the temperature down.

The container you are trying to cool will be one of two types – insulated or uninsulated.

With an insulated container you want to be sure the exposing fire is actually heating the tank as applying water to a tank containing a cryogenic will in effect attempt to warm the contents, and the only reason you would apply water would be to absorb the extreme heat of the fire.

If you are fortunate enough to be facing an insulated container, you will have one thing going for you; the fact that the insulation will slow down the transfer of heat from the fire to the contents or even to the pressure vessel.

This is not the case with a uninsulated container. There will only be a thin layer of steel or aluminum between the fire and the contents. If you do nothing or your actions are not sufficient to keep the container or its contents at a safe temperature, the situation will get worse and you may not even realize it.

The contents of the container may be either a compressed gas or a liquefied gas.

If it is a compressed gas, the pressure will rise and hopefully the relief valve will open and prevent the container from failing. However, the container could fail due to the extreme heat of the fire. In any case, there will be a release of gas. Remember, some poisonous gases are not allowed to have pressure relief valves.

If the contents are a liquefied gas, the relief valve may still operate to relieve the pressure. However, if the container fails, the released gas will be much more destructive and disastrous than the compressed gas release. The failure even has a name, BLEVE, which will be discussed in the next part of the program.

To summarize, let's just go back over the main hazard points.

The gas hazard will be either inside or outside of the container. If outside of the container, there will be either no fire or a fire condition. If a no fire situation there will be one of four hazards: a cryogenic hazard, an asphyxiant hazard, a toxic hazard, or a combination of these. If it is a combustion hazard, it will be either indoors or outdoors.

If it is an inside container hazard, the problem will usually be from an exposure fire. The gas will be either in an uninsulated or an insulated container. An insulated container buys you a bit more time. The gas will either be a compressed gas in which the end result will be a gas release or it will be a liquefied gas in which case the end result could be a BLEVE.

BASIC & COMBINED GAS LAWS

BOYLES LAW:

When the temperature is kept constant, the volume of a gas is inversely proportional to the pressure upon it.

CHARLES LAW:

When the external pressure is kept constant, the volume of a gas is directly proportional to its absolute temperature.

BASIC AND COMBINED GAS LAWS

A knowledge of the basic concepts of gaseous behavior is vital to your understanding of what action should be taken during an emergency situation involving a confined gas, and why.

For our purposes at this time, only those laws concerning the reactivity of gases to such stimuli as heat and volume are important. These laws are basically the result of experiments done separately by two scientists, Robert Boyle and Jacques Charles.

Boyle was concerned primarily with the relationship of pressure and volume to a gas. His experimentation proved that the pressure of a contained gas is directly proportional to the volume of space in the container. Therefore, by filling a one cubic foot container with gas at atmospheric pressure and then halving the volume to 1/2 cubic foot, we have also doubled the pressure. It is this principle that is put to use when air is compressed to fill a SCBA bottle.

Jacques Charles, on the other hand, experimented with the effect of heat on the pressure of a confined gas. His work proved that, put into the simplest of terms, as the heat of a confined gas rises, so will the pressure. Therefore, by applying sufficient heat to a properly designed sealed container of gas we will eventually raise the pressure enough to cause the relief valve to open and thus relieve the pressure on the container structure.

By combining both of these principles we now have a basis for understanding when dealing with a confined gas. We know that there is a very direct relationship among pressure, temperature, and volume in working with a gas. By confining a gas in a given volume and applying heat, for instance, either the pressure must increase or the volume must expand. When we discuss increasing heat of a gas, confined in a container, with elasticity, such as a balloon, we can safely discuss increasing volume to a point. When we're discussing a container such as a storage container or cylinder, an increase in heat would cause an increase in pressure.

An understanding of this principle should provide some insight into the hazards involved when the conditions of gas confinement are not normal or as designed.

COMMON PROPERTIES BASIC TO ALL GASES
(The Science of Gases)

Since the beginning of man's existence, he has had to learn to live and work with the matter that nature has placed on this earth.

As time went on, he learned to alter this matter so that it was in a form that better suited his needs and to improve his standard of living.

Even though this ability to alter matter appears to be a human accomplishment and, in a sense indeed it was, man still had to adhere to basic laws to nature.

As we progress into this course, many of the theories, concepts and principles we will be discussing will be better understood if you have some basic understanding of these laws.

We begin with a look at the two basic properties of concern to the Firefighter, the physical property and the chemical property of matter.

The physical property is the size, shape and form in which a substance exists.

The chemical property is the ability a substance has to react with other materials.

Since all matter does exhibit the physical and chemical properties, and since a fire is exhibiting both of these properties out of control, let's discuss them one at a time.

The physical property of matter determines that matter can exist in three states: The solid state, the liquid state, and the gaseous or the vapor state. There are two factors that govern which state any given substance will be in. One being temperature and the other being pressure. Again, we see two of the factors in Boyle's and Charles' experiments. The means of altering physical state by temperature change is experienced quite frequently in our daily lives. In fact, man has learned to use this process for his convenience. We lower the temperature of water below 32° F (0° C) to freeze or make the water into the solid state, which we commonly call ice. We use this, for example, to cool our drinks or as a playing field for sporting events. When this condition occurs naturally in our environment, it even hinders us at our job of fighting fires.

Water in the liquid form exists at temperatures between 32° F (0° C) and 212°F (100° C). This state is necessary to sustain life. We also use this liquid to extinguish fires. When we raise the temperature of water above 212° F (100° C) at atmospheric pressure conditions, it turns to the gaseous state, or steam as it is called. We also use this process in firefighting. Man has also learned to trap this water vapor in a container and, by continuing to raise its temperature, it creates a pressure higher than atmospheric. This proved to be a significant discovery as he learned to power machinery to make his life easier. This process was also used in firefighting for a considerable period of time.

It is not always to our advantage to alter physical state by changing the temperature. In which case, we have an alternative means, that being a pressure change.

The process of changing physical state by altering pressure centers around two areas, altering the melting point or the boiling point of a substance. The melting point has little significance in our study of gases in this course; however, the boiling point does, and therefore, we will center our discussion only around the boiling point.

The normal boiling point of a liquid is the temperature of the liquid at which its vapor pressure equals the atmospheric pressure. We can raise the temperature at which a liquid boils by confining the vapor in a container and allowing the pressure to increase, or by increasing the pressure with a mechanical compressor.

One point to remember "at atmospheric pressure (14.7 PSI) no substance can exist as a liquid if the temperature of the substance is above its boiling point".

Now that we have explored the physical state and the conditions of those states, we can now define a gas. By definition, a gas is one of the physical states of a substance.

There is a very specific and scientific definition of a gas. For our purposes and for general uses, we can use this simplified definition:

> *"A gas is a substance that exists only in the vapor or gaseous state at normal atmospheric pressure conditions approximately 50° to 70° F (10° to 21° C)."*

Remember this is overly simplified and there maybe some exceptions; however, nearly all gases fall in this category and as you can see their boiling points would be lower than 50° to 70°F. This condition can be referred to as N.T.P. or normal temperature and pressure conditions.

The next point we must make clear is that when we condense any substance from its gaseous state to its liquid state, the volume of space it occupies is reduced quite significantly. At atmospheric pressure condensing steam to liquid reduces its volume by approximately $1/1700^{th}$ of its original volume.

If we consider the fact that when we store and transport any substance, the goal or objective is to get the most amount of material in the smallest container possible. Therefore, storing and transporting gases in the liquid rather than the gaseous state is much more convenient and economical.

Here we can establish some ground rules. To store and transport a gas as a liquid we must do one of two things. We must either lower the temperature of the liquid to or below its boiling point at atmospheric pressure, or raise the pressure to equal its respective vapor pressure at the liquid's ambient temperature. When we store and transport gases as a liquid they fall into one of three categories: (1) Pressurized liquefied gases (liquid at ambient temperature and moderate to high pressure), (2) Refrigerated liquefied gases (gases that need only be refrigerated to a moderate degree and with pressure from atmospheric to a few pounds), (3) Cryogenic liquefied gases (gases that need only be refrigerated to a very low temperature).

Naturally, the last two would have to be stored and transported in insulated containers to prevent the liquid from warming to ambient temperature, while the first one can be transported in uninsulated containers allowing it to remain at ambient temperature.

There are important points to remember, as there will be two distinctly different methods of handling an incident based on those points.

Some examples of Pressurized Liquefied gases are LP gases, Chlorine, Ammonia, Vinyl Chloride, and others, where the pressure will vary from about 3 or 4 PSI to about 120 PSI at 70°F depending on the gas.

An example of a Refrigerated Liquefied gas is Refrigerated Propane where the temperature would be -44° F at atmospheric pressure (14.7 PSI).

Some examples of Cryogenic Liquefied gases are Liquefied Natural gas (methane), Liquid Oxygen, Liquefied Argon and Liquefied Hydrogen. The temperature of these gases will vary from about -450°F to -150°F at atmospheric pressure (14.7 PSI).

Not all gases are stored and transported in the liquid state, many cannot be liquefied without being reduced in temperature, and therefore they are sometimes bottled at normal temperatures and are only in the gaseous state. When we store them in this manner we call them compressed gases. Some examples are: Compressed air, Oxygen, Argon, CO_2, etc.

When a substance reacts with itself to either decompose or polymerize, or when it reacts with another substance to satisfy its need to link up with something or to form a new substance, one or both of two things occur in relationship to gases.

One, large quantities of heat are produced, this is called combustion or fire, or two, there will be a physiological effect on living things (toxic effect or poisoning).

The heat effects of the Chemical reaction of propane with oxygen (fire) is one example, and the physiological effects of carbon monoxide gas are all too familiar to the Firefighter.

To recap the major points of this presentation:

1. Matter has two basic properties of concern to the Firefighter:
   a. Physical
   b. Chemical

2. The physical property has three states:
   a. Solid
   b. Liquid
   c. Gaseous

3. The two factors that govern physical states are:
   a. Temperature
   b. Pressure

4. A gas is a substance whose physical state is the gaseous state at atmospheric pressure (14.7 PSI) and normal temperature 50 to 70°F. (This is called normal temperature and pressure - N.T.P.)

5. Gases may be stored in their containers as a:
   a. Pressurized liquid
   b. Refrigerated liquid
   c. Cryogenic liquid
   d. Compressed gas

6. The chemical property of matter may produce:
   a. Large quantities of heat
   b. Toxic effect on living things

The better your understanding of these concepts the more likely your actions will not result in disaster.

DEFINITIONS

A.P.I.: American Petroleum Institute

A.S.M.E.: American Society of Mechanical Engineers

BLEVE: Boiling Liquid Expanding Vapor Explosion – major container failure into two or more pieces, at a moment in time when the contained liquid is at a temperature well above its boiling point at normal atmospheric pressure. A portion of the liquid is vaporized (often 1/3 – 1/2), and this large liquid-to-vapor expansion provides tremendous energy. *NOTE: May occur even though relief valve is operating!*

BOILING POINT: The boiling point of a liquid is the temperature at which its vapor pressure equals the atmospheric pressure - the temperature at which a liquid becomes a vapor or a gas.

BULK PLANT: A property where flammable liquids or gases are delivered by tanker ship.

CRITICAL PRESSURE: The pressure required to liquefy a gas at its critical temperature.

CRITICAL TEMPERATURE: The temperature above which a gas cannot be liquefied by pressure alone - The temperature above which the material can exist only in a gaseous state.

D.O.T.: Department of Transportation (U.S.)

FIRE POINT: Temperature at which a liquid gives off enough vapor to continue to burn when ignited - usually a few degrees higher than the flash point.

FLASH POINT: The minimum temperature of a liquid at which it gives off vapor in sufficient quantity to form an ignitable mixture with air near the surface of the liquid or within the vessel used. The mixture will not support continuous combustion until or unless the fire point is reached.

FLAMMABLE OR EXPLOSIVE LIMITS: The lower limit (LEL) is the minimum concentration of gas or vapor in air below which a substance does not burn when exposed to an ignition source. The upper limit (UEL) is the maximum concentration of the substance in air above which ignition does not occur. The lower and upper limits are usually expressed in percent by volume of vapor in air.

IGNITION TEMPERATURE (Auto Ignition Temperature):
The minimum temperature required to initiate or cause self-sustained combustion independently of the heating or heated element. The temperature at which the substance will ignite without any additional ignition source.

LIQUIFICATION: A process whereby a gas becomes a liquid when compressed OR both compressed and cooled.

LNG: Liquefied Natural Gas: A mixture of materials all composed of carbon and hydrogen. The principal component is methane (83%-99%) with lesser amounts of propane, ethane, and butane. LNG is nontoxic, but is an asphyxiant.

Approximate Properties:
Normal boiling point (NBP)..-260° F.
Density of liquid at NBP...3.5 lbs. per gallon
Density of vapor at NBP (compared w/air at 70° F).........1.47
Liquid to vapor expansion...600 to 1
Flammable range...5 - 15%

LNG is shipped as a cryogenic gas in insulated cargo trucks or marine vessels. It is stored in insulated ASME Code or API tanks.

LPG: Liquefied Petroleum Gas: A mixture of materials all comprised of carbon and hydrogen. Applied to that segment of the gas family, which is a vapor at atmospheric pressure and normal temperature, but under conditions of moderate pressure can be changed to a liquid. Propane, Iso-butane, normal butane, or mixtures of these three are referred to as Liquefied Petroleum Gases. (Also referred to as LPG or LP Gas).

Approximate Properties

		Commercial Propane	Commercial Butane
Vapor Pressure in PSIG at	*70 °F*	*120 psi*	*17 psi*
Vapor Pressure in PSIG at	*100 °F*	*205 psi*	*37 psi*
Vapor Pressure in PSIG at	*130 °F*	*300 psi*	*69 psi*
Specific Gravity of Liq. at	*60 °F*	*.509 psi*	*.582 psi*
Weight per Gallon liquid at	*60 °F*	*4.24 lbs*	*4.81 lbs*
Specific Gravity of Vapor at	*60 °F*	*1.52*	*2.01*
Boiling Point @ 14.7 psi		*-44 °F*	*32 °F*
Flammable Limits	*Lower*	*2.15%*	*1.55%*
	Upper	*9.60%*	*8.60%*

Liquefied Petroleum Gas (LPG), in domestic and recreational applications, is sometimes known as "bottled gas", and is shipped as a liquefied gas in uninsulated DOT and CTC cylinders and ASME tanks and in DOT specification cargo trucks, railroad tank cars and marine vessels.

NTP: Normal temperature and pressure: 55-70° F at 14.7 PSI.

SPECIFIC GRAVITY: The ratio of the weight of a solid or liquid substance to the weight of an equal volume of water. The specific gravity of water is considered as one (1). A solid or liquid with a specific gravity less than one (1) will float on water. If more than one (1), it will sink.

$$\textit{Specific Gravity} = \frac{\textit{Weight of substance}}{\textit{Weight of equal volume of water.}}$$

TRIPLE POINT: Point at which a substance can exist as a solid, gas, or liquid by manipulating temperature & pressure.

VAPOR DENSITY: Density of a gas or vapor compared to an equal volume of dry air. Air is rated as one (1). A figure greater than one (1) indicates the gas or vapor is heavier than air, a figure less than one (1) indicates it is lighter than air. (Vapor density figures do not always indicate behavior of vapor!)

$$\textit{Vapor Density} = \frac{\textit{Molecular weight of a gas}}{\textit{29 (MW air)}}$$

VAPOR PRESSURE: In a closed container the motion of the molecules leaving the surface of the liquid is confined to the vapor space above the surface of the liquid. As an increasing number re-enter the liquid, a point of equilibrium is eventually reached when the rate of escape of molecules from the liquid equals the rate of return to the liquid. The pressure exerted by the escaping vapor at the point of equilibrium is called vapor pressure.

VAPOR SPACE: That space above the liquid level in an enclosed tank. Whenever a tank is filled, a certain percentage of the capacity of the tank must be left unfilled to allow for expansion of the liquid contents. The percentage of capacity a tank may be filled is governed by size, location, and type of tank, as well as the type of product. The tank should not be allowed to become "liquid full" as only a slight temperature rise may cause the relief valve to open and discharge liquid! Liquid propane expands at the rate of 1.6% for each 10° F rise in temperature.

FLAMMABLE OR EXPLOSIVE RANGE: The numerical difference between the upper and lower flammable (or explosive) limits. *Example:* Acetylene has a LEL of 2.5%, Acetylene has a UEL of 81%, and Acetylene has a range of 78.5%. *NOTE: When the mixture temperature is increased, the range widens.*

GAS: Substance which exists in the gaseous state at so-called "NTP" (approximately 70° F and 14.7 PSI). A gas would be considered a substance or mixture of substances which, when in the liquid state, would exert a vapor pressure of 40 PSI or greater at 100° F as compared to a flammable liquid having a vapor pressure not exceeding 40 PSI at 100° F ("Gas": Gaseous material existing above the Critical Temperature. "Vapor": Gaseous material existing below the Critical Temperature).

CLASSED BY CHEMICAL PROPERTIES:

1. *Flammable Gases:* Any gas which will burn in the concentration of oxygen in the air.
2. *Nonflammable Gases:* The many gases which will not burn in any concentration of air or oxygen - a number of these gases will support combustion ("oxidizers" such as oxygen), while some such as nitrogen, argon, helium, etc. will not support combustion ("inert" gases).
3. *Reactive Gases:* Gases which will either react with other materials or within themselves by a reaction other than burning and under reasonably anticipated initiating conditions of heat, shock, etc. *Examples: Chlorine, fluorine, acetylene, vinyl chloride, etc.*
4. *Toxic Gases:* Gases that are poisonous or irritating when inhaled or contacted. Ammonia, carbon monoxide, hydrogen sulfide, etc. are examples.

CLASSED BY PHYSICAL PROPERTIES:

1. *Compressed Gases:* Those which at normal atmospheric temperatures inside their containers, exist solely in the gaseous state under pressure. The pressure is basically dependent upon the pressure to which the container was originally charged and upon how much gas remains.
2. *Cryogenic Gases:* Liquefied gases which exist in their containers at temperatures far below normal atmospheric temperatures, usually slightly above their boiling point at normal pressure, and correspondingly low to moderate pressures.
3. *Liquefied Gases:* Those which at normal atmospheric temperature inside their container, exist partly in the liquid state and partly in the gaseous state, and under pressure as long as any liquid remains in the container.

CLASSED BY USAGE:

1. Fuel Gases
2. Industrial Gases
3. Medical Gases