Technically Speaking

BOILING POINTS, VAPOR PRESSURES, MELTING POINTS, FLASH

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One of the questions AristaTek has been asked is why databases sometimes give different answers for boiling points, melting points, flash points or other physical properties. Maybe the number displayed in the PEAC tool is different than a number located from an Internet source or a manual.

Let us consider a couple of examples. Methyl Isocyanate is the chemical that was released in the 1984 Bhopal India incident, which killed approximately 1850 people. Pulmonary edema (fluid in the lungs) from inhaling the chemical was the major cause of death. The PEAC tool lists the melting point of methyl Isocyanate as –112° F (-80°C). The boiling point is listed as 102°F (39°C), and the flash point is listed as 0° F (-18°C). The NIOSH Pocket Guide lists the boiling point as 139° F and the flash point as 19°F but does not give a number for melting point. The CHRIS Manual lists the boiling point as 102.4°F, the melting point as <-112°F, and no flash point. The Handbook of Chemistry and Physics (69 ed) lists the melting point as –45°C (-49° F) which is very different from the CHRIS Manual number of <-112°F. Checking various Internet sources brings up several additional numbers or verification of numbers in the NIOSH or CHRIS Manual. The NIST database lists the boiling point as 102°F (39°C). When AristaTek selected numbers to display in the PEAC tool from the many available references sources, AristaTek recognized that the users would be Emergency Responders, and therefore the most conservative number should be displayed if there is disagreement. Unless there is some overriding consideration, the lowest melting point, the lowest flash point, and the lowest boiling point will be displayed if there is disagreement between the reference sources.

Chlordane is a chlorinated organic pesticide. Technical grade chlordane pesticide is a mixture of about 26 different compounds, some of them isomers and some of them various compounds with different amounts of chlorine or different molecular weights. A typical mixture of technical grade chlordane is 24% trans-chlordane, 21.5% various chlordane isomers, 19% cis or alpha-chlordane, 10% nonachlor, and 18.5% other constituents. The commercial product may contain kerosene or it may contain a solid absorbent material. We are not dealing with a material with a unique physical form, a definite melting point or boiling point, or a flash point. The boiling point for cis-chlordane is 107°C (224°F), but each component of chlordane has its own boiling point. Its physical form may be a colorless or amber or brown viscous liquid or a white crystalline powder or granules. It may be nearly odorless or have a strong chlorine-like odor. Some published numbers for flash points are 132°F and 225°F, but the flash point could be less than 75°F. Some UN or NA Shipping Numbers used by the Dept. of Transportation for shipping chlordane are:

NA 2762: Chlordane, liquid

UN 2761: Organochlorine pesticides, solid, toxic, not otherwise specified

UN 2762: Organochlorine pesticides, liquid, flammable, toxic, not otherwise specified, flash point less than 23°C

UN 2995: Organochlorine pesticides, liquid, toxic, flammable, not otherwise specified, flash point 23°C or more

UN 2996: Organochlorine pesticides, liquid, toxic, not otherwise specified

Chlordane is a classic example of a material which is a mixture of many components which can display different physical properties depending upon the composition.

Boiling Points and Vapor Pressures

Water boils at 212°F (100°C). Right? There are situations where water boils at some other temperature. The boiling point of water at 212°F (100°C) is true only at sea level elevation and if the water is not contaminated with other chemicals. Let us construct a table expressing absolute pressure as a function of elevation. We can use any units we want to express pressure (e.g. atmospheres, mm Hg, pounds per square inch (psi), or kilopascals).

Elevation, feet	Atm pressure [sea level = 1]	mm Hg pressure
0	1.000	760
1000	0.964	733
2000	0.929	706
3000	0.896	681
4000	0.864	657
5000	0.832	632
6000	0.802	609
8000	0.741	564
10000	0.688	533
12000	0.639	486
15000	0.565	429
20000	0.460	350
30000	0.297	226
40000	0.186	141

A chemical will boil when its vapor pressure equals the atmospheric pressure. Let us look at the water example. We will construct a table listing vapor pressure of water as a function of temperature.

Temperature, °F	Vapor pressure of water, atm	Vapor pressure of water, mm Hg
212	1.000	760
210	0.961	730
200	0.785	597
190	0.635	483
180	0.511	388
170	0.407	310
160	0.323	245
150	0.253	192

This article is being written in Laramie, Wyoming, where the elevation is 7300 feet. The atmospheric pressure is 0.762 atm. Water at Laramie elevation boils at about 198°F and not at 212°F.

The PEAC tool displays the normal boiling point, that is, the temperature at which the chemical boils at 1 atm pressure (sea level). It also displays the chemical vapor pressure in atmospheres usually at 68°F but sometimes at some other temperature.

For example, the normal boiling point of benzene is 176°F and the vapor pressure of benzene at 68°F is 0.1 atm. What does this 0.1 atm vapor pressure at 68°F mean? It means that if several gallons of benzene were spilled in a room, some of the benzene will evaporate into the air. At 68° F, the benzene concentration in the air could reach 10% by volume if the room were completely sealed. The Upper Explosive Limit for benzene is 7.8% and the Lower Explosive Limit for benzene is 1.2%. At first glance, it might appear that the concentration in the room will exceed the upper explosive limit of 7.8%, but remember that it takes time for the concentration to build up and there is probably enough ventilation to keep the concentration below 7.8%. Also, benzene is a recognized carcinogen. The NIOSH 8-hour recommended exposure limit for benzene is only 0.1 ppm. A 0.1 atm vapor pressure is equivalent to 10000 ppm concentration for a spill in a sealed-up room.

Example: A 1-gallon container of acetone falls off a storage shelf in a closet and spills. Assuming that the closet is poorly ventilated, what conditions can be expected in the closet?

Solution: The NIOSH Pocket Guide lists the vapor pressure under normal ambient temperature at 180 mm of Hg. The boiling point is 133°F. The Lower Explosive Limit is 2.5%. The Upper Explosive Limit is 12.8%. The Flash Point is 0°F. The NIOSH recommended 8-hour exposure limit is 250 ppm. The PEAC tool gives the same information except the vapor pressure is listed as 0.236 atm at 68°F. The vapor pressure in atmospheres can be converted to mm of Hg by multiplying by 760, e.g., 760 x 0.236 = 179.4 mm Hg which is the same as the NIOSH Pocket Guide. If the room were fully sealed, acetone vapors could build up to 23.6% concentration. In actuality, there will be some ventilation, and the closet could have an explosive mixture of acetone vapor (between 2.5 and 12.8%). Concentrations will be well above the 8-hour exposure limit of 250 ppm.

Remember that ppm means "parts per million". A 10% concentration of vapor in air is equivalent to 100,000 parts per million (ppm). A 10% concentration of vapor in air is also equivalent to a vapor pressure of 0.1 atm at sea level, or 76 mm Hg.

Suppose the 1-gallon container was spilled near Leadville, Colorado at 10,000 ft elevation. The vapor pressure of acetone at 68°F is still 180 mm Hg, but the total atmospheric pressure is 533 mm Hg. If the room were completely sealed, acetone concentrations could build up to 180/533 (100%) = 33.8%. The acetone would also vaporize faster because of the reduced total pressure.

The vapor pressure of a chemical increases with temperature. The PEAC tool contains internal files which express vapor pressure as a function of temperature for many chemicals. The information is not displayed to the PEAC user but is used to calculate evaporation rates of spilled chemicals.

<u>Boiling Point of Gasoline</u>

Gasoline as used by vehicles is a mixture of roughly 230 different chemicals. Gasoline formulations vary depending upon the location, time of the year, environmental regulations, and availability. If the PEAC user looks up the boiling point of gasoline on the PEAC tool, the temperature 102^{o} F (or 39^{o} C) is displayed. But the information is misleading. Gasoline boils over a range of temperatures, with the most volatile components starting to boil away at roughly 102^{o}F. The less-volatile components will boil at higher temperatures. Gasoline boils over range of temperatures, between 39 and 200^{o} C (102^{o}F and 392^{o} F) typically, the temperature range varies depending upon the formulation. The final boiling point of the last residual of gasoline might be typically 225^{o}C (437^{o}F). This is in contrast to a pure chemical such as heptanes (one of the components of gasoline) which boils at a single temperature (209^{o} F; 98^{o}C).

Petroleum refining begins with the distillation of crude oil into fractions of different boiling ranges, usually called "light naphtha", "heavy naphtha", "kerosene", "light gas oil", "heavy gas oil", and "reduced crude". The naphtha fractions obtained by distillation are also called "virgin naphtha" or "straightrun gasoline". The hydrocarbon products obtained by distillation depend greatly upon the type of crude oil being distilled. Kerosene and light gas oil fractions (also called middle distillates) are used in the production of kerosene, jet fuel, diesel fuel, and furnace oils. The heavy gas oil may be used for heavy diesel fuel, industrial fuel oil, and bunker fuel. All of these are mixtures of various hydrocarbon compounds with a range of boiling points. If the PEAC user looks up the boiling point for fuel oil, jet fuel, naphtha, or other petroleum distillate, a single temperature is displayed representing a temperature at the lower end of the boiling point range.

The lower boiling point hydrocarbon distillates are more valuable because they are major components of gasoline. A major petroleum refining step is hydrocracking, where higher boiling hydrocarbons are broken down or cracked forming lower boiling point hydrocarbons. The higher boiling point hydrocarbons are subjected to hydrogen and heat in the presence of a catalyst which results in the formation of lower molecular weight, lower boiling point hydrocarbons. The catalyst, which becomes fouled with carbon, is regenerated.

A typical breakdown of modern gasoline (excluding additives and oxygenated compounds) might be 15% n-paraffins (examples: pentane, hexane, heptane, octane, decane, etc.); 30% iso-paraffins (examples: 1-methylpropane, 2-methylbutane, 2,2,3-trimethylbutane, etc.); 12% cycloparaffins (example: cyclohexane, cyclopentane, etc.); 35% aromatics (examples: benzene, toluene, ethyl benzene, 1,3,5-trimethylbenzene; m-xylene, etc.); and 8% olefins (examples: 2-pentene, 2-methylbutene, cyclopentene, etc.). The octane number of the gasoline is a function of the components.

The U.S. Environmental Protection Agency has specified that gasoline contain a minimum of 2% oxygen by weight to reduce automotive emissions and improve air quality in polluted areas. This can be done by adding alcohols, notably ethanol, to gasoline to supply the oxygen component. Until recently, refiners have added methyl tert-butyl ether (MTBE) to gasoline to supply the oxygen component; a gasoline composition of 12% MTBE would meet the 2% oxygen by weight requirement. But MTBE proved to be a dangerous pollutant itself, contaminating groundwater from leaking gasoline tanks at fuel stations.

Modern refiners add detergents (usually an amide compound and alkylammonium dialkyl phosphate to prevent the formation of contaminants in the carburetor or fuel injectors. Light lubricants may be added to help lubricate cylinders and top piston rings. Deicing and anticorrosion additives are also in modern gasolines. Organic dyes are also added to identify brands and grades of gasoline.

In summary, gasoline is a mixture of many different chemicals. Many of the components of modern gasoline are also individually listed in the PEAC tool. The mixture boils over a temperature range rather than at a single temperature. .

Sublimes

The PEAC user will sometimes encounter the word “sublimes” or “undergoes sublimation” when checking the melting point or boiling point of some chemicals. A solid heated will convert directly to the gas phase at this temperature without forming a liquid, or conversely, the gas condenses as a solid when cooled. An example is dry ice which converts to carbon dioxide gas when left out in the open without forming a liquid. Liquefied carbon dioxide exists but only at high pressure. .

Decomposes

Sometimes this note is displayed in the PEAC tool after the melting point or boiling point temperature. As the word implies, the chemical decomposes when heated to this temperature. The chemical does not reform if cooled.

Flash Point

The flash point is lowest temperature at which a liquid can form an ignitable mixture in air near the surface. The lower the flash point temperature, the easier it is to ignite.

Flash points are determined experimentally by heating the liquid in a container and then introducing a small flame just above the liquid surface. The temperature at which there is a flash/ignition is recorded as the flash point.

Some of the chemicals in the PEAC tool may be gases at ambient temperature, but a flash point is listed. In this situation, the gas is chilled forming a liquid, and the liquid is heated with the flame present.

Two methods are recognized for measuring the flash point. The first is the closed-cup method in which the vapors are prevented from escaping. The second method is the open-cup method in which the vapors are allowed to escape. The two methods often give different answers. Usually the closed cup method gives the lower temperature results. The PEAC tool displays the lower temperature when several values are published.

The CHRIS Manual [CHRIS = Chemical Hazards Response Information System] published by the U.S. Department of Transportation and U.S. Coast Guard] lists both closed cup and open cup flash points for many chemicals. Examples are listed in the following table:

Table 1: Open Cup and Closed Cup Flash Points for Example Chemicals

Chemical	Open Cup, ^{o}F	Closed Cup, ^{o}F
Benzyl alcohol	220	213
n-Butyl Acetate	99	75
Cyclohexanone	129	111
p-Cymene	140	117
Diacetone alcohol	142	125

1,2-Dichloropropane	70	60
Methanol	61	54
Methyl isobutyl ketone	75	73
Trimethyl phosphite	130	82

The American Society for Testing and Materials (ASTM) has published procedures for the determination of flash points.

ASTM D56: Closed Cup; Flash Point by Tag Closed Tester

ASTM D93: Closed Cup; Flash Point by Pensky-Martens Closed Cup Tester

ASTM D92: Open Cup; Flash Point by Cleveland Open Cup Tester

OSHA’s 1910.106 (a)(14) regulations for measuring flash points specify the Tag Closed Tester for the closed cup method for chemicals with a viscosity less than 45 SUS at 100°F and does not contain suspended solids nor does not have a tendency to form a surface film. Otherwise the Pensky-Martens Closed Tester shall be used for the closed cup method.

Even though the procedure for measuring flash points has been standardized, different researchers can come up with different results. Add to this the complexity of measuring the flash point of mixtures (e.g. gasoline, fuel oil, etc.) where the individual components have different volatilities and flash points. The measurement of flash points of organic peroxides is particularly troublesome because they undergo auto-accelerated thermal decomposition when heated. It should not come as a surprise when different reference sources often give different temperatures for flash points.