The Case of the FATAL TANK ENTRY

By Mitch Ricketts

Math Toolbox is designed to help readers apply STEM principles to everyday safety issues. Many readers may feel apprehensive about math and science. This series employs various communication strategies to make the learning process easier and more accessible.

Workers may be overcome by hazardous vapors while opening hatches and entering chemical storage tanks. Details surrounding one such event are depicted in Figure 1. Vapors are produced when volatile liquids evaporate. When inhaled, some vapors may cause asphyxiation, severe inflammation of respiratory tissues, systemic poisoning or sudden death.

Safety professionals can help protect workers by learning to recognize potentially toxic exposures. Lessons from the fatal New Jersey tank entry provide the basis for several exercises to help readers identify hazardous vapor concentrations associated with chemical storage tanks.

How Can an OSH Professional Predict Vapor Concentrations in Chemical Tanks to Prevent Confined Space Entry Deaths?

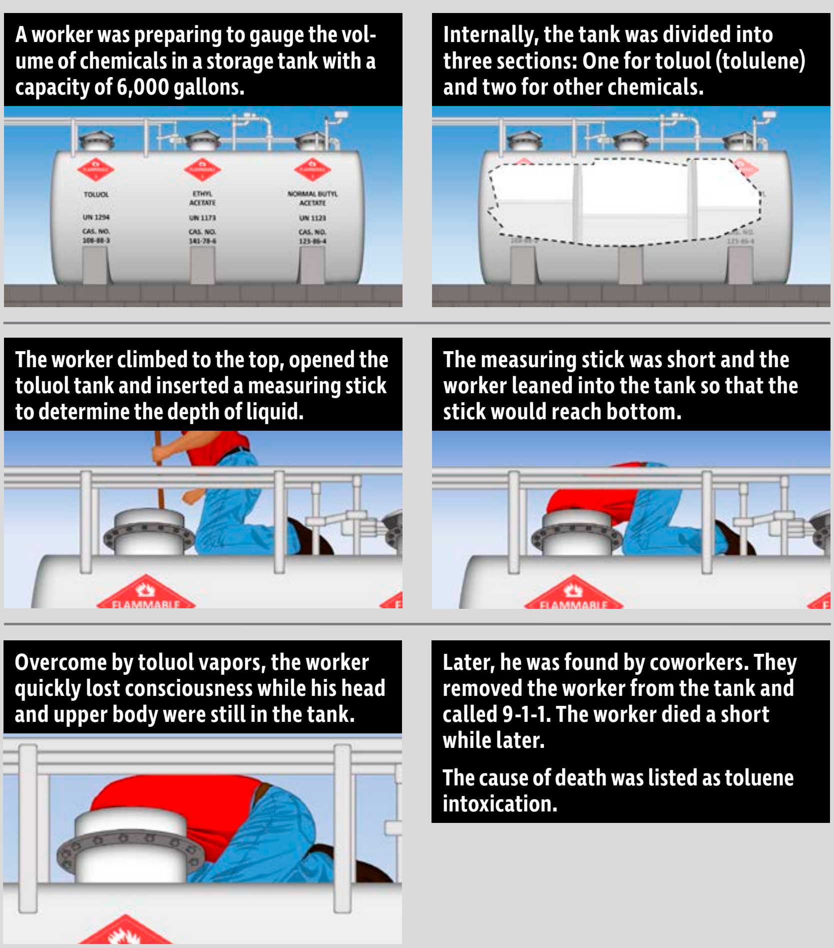
In confined spaces, workers may be exposed to hazardous vapors in the "headspace," which is the area above the liquid in a tank (Figure 2). The airborne concentration of vapors in the headspace depends on several factors, including:

- Temperature of the liquid. All else being equal, warmer liquids tend to produce more vapor.
- Absolute barometric pressure inside the vessel. Liquids generally release more vapor when barometric pressure in the headspace is low. Absolute barometric pressure is the sum of a) pressure in the environment outside the tank (atmospheric pressure); and b) any positive or negative pressure within the tank (gauge pressure).
- Volatility of the liquid, as reflected by its vapor pressure. Highly volatile liquids have higher vapor pressures and tend to release more vapor. In the current application, vapor pressure is the pressure of vapor within the chemical storage tank.
- Purity of the volatile liquid. Some additives may increase vapor production, while others may reduce it.
- Size of the headspace and duration that the tank has been closed. It may take some time for vapors to fully saturate the headspace after a tank is closed. However, headspace size and duration become irrelevant once the vapor concentration reaches equilibrium with the liquid.

Equation for Maximum Vapor Concentration Within a Container

We can predict the maximum (worst-case) concentration of vapor in a closed tank of liquid using the equation for headspace saturation vapor concentration:

FIGURE 1
TOXIC EXPOSURE, NEW JERSEY, 2013



Note. Adapted from "Batch Maker Dies After Toxic Exposure to Toluene Vapor" (New Jersey FACE investigation report No. FACE 13-NJ-059), by New Jersey Department of Health, 2015.

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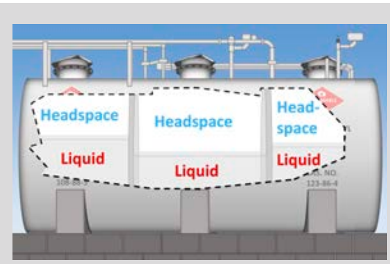
FIGURE 2
HEADSPACE WITHIN A LIQUID STORAGE TANK



$$C = \frac{P_v \cdot 10^6}{P_b}$$

where:

C = airborne concentration of vapor in the headspace of a tank or container, in parts per million (ppm)

P_v = vapor pressure of the contaminant at a specific temperature, measured as gauge pressure (P_{Gauge})

P_b = absolute barometric pressure in the headspace of the container (in the same metric used for P_v). Since absolute pressure is the sum of gauge and atmospheric pressures, $P_b = P_{Gauge} + P_{Atmosphere}$

10^6 = constant for converting decimal fraction to ppm

How Do I Use the Formula for Maximum Vapor Concentration?

As in the fatal tank exposure, imagine a tank containing liquid toluol. We can find the vapor pressure of toluol by checking the safety data sheet (SDS), or by consulting sources such as the *NIOSH Pocket Guide to Chemical Hazards*, available on the NIOSH (2007) website. According to the guide, the vapor pressure of toluol is 21 millimeters of mercury (21 mm Hg gauge). Note that vapor pressure varies according to temperature, and vapor pressures in the *NIOSH Pocket Guide* are normally calculated at 68 °F (20 °C). This means our calculation will be valid only if the actual temperature of liquid in the tank is 68 °F (we will consider temperature-based corrections later).

Besides vapor pressure, we also need to know the absolute barometric pressure in the tank. Absolute pressure is the sum of gauge pressure and atmospheric pressure (Figure 3). We can read gauge pressure directly from a gauge on the tank (if so equipped). Atmospheric pressure can be read from a barometer outside the tank, or we can look it up in real time for our location on National Weather Service's (NWS) website, **www.weather.gov**. For the purposes of this example, let's say the pressure gauge on the tank reads zero, meaning that pressure inside the tank is the same as atmospheric pressure (we will consider other pressure conditions later). Let's also imagine that upon checking with NWS, we find that the atmospheric pressure for our location at this time is 760 mm Hg. To calculate absolute barometric pressure within the tank, we add gauge pressure (0 in this case) to atmospheric pressure (760 mm Hg in this case), as follows: $P_b = 0_{Gauge} + 760_{Atmosphere} = 760$ mm Hg absolute.

We now have all the data needed to calculate the maximum concentration of toluol vapor in the tank at this temperature and pressure. Specifically, this is what we know:

- The vapor pressure of toluol is 21 mm Hg gauge at our temperature of 68 °F (20 °C). This is the value of P_v in the formula.
- The absolute barometric pressure within our tank is 760 mm Hg absolute. This is the value of P_b in the formula.

We solve the problem as follows:

Step 1. Start with the equation for headspace saturation vapor concentration:

$$C = \frac{P_v \cdot 10^6}{P_b}$$

where:

C = airborne concentration of vapor in the headspace in ppm

P_v = vapor pressure of the contaminant

P_b = absolute barometric pressure in the headspace

Step 2. Insert the known values for vapor pressure of toluol (21 mm Hg gauge, at 68 °F) and absolute barometric pressure inside the tank (760 mm Hg absolute). Then solve for maximum headspace vapor concentration (C):

$$C = \frac{21 \cdot 10^6}{760} = 27{,}631.58\ ppm$$

Step 3. Our calculation indicates the worst-case concentration of toluol vapors within the tank may reach 27,631.58 ppm, assuming the temperature and pressure in the tank are 68 °F and 760 mm Hg absolute, respectively. Checking the *NIOSH Pocket Guide*, we find the immediately dangerous to life and health (IDLH) concentration for toluol is 500 ppm. IDLH is the maximum airborne concentration from which a worker can be expected to escape without injury or irreversible health effects if respiratory protection equipment fails. The calculated maximum headspace concentration in this case (27,631.58 ppm) far exceeds the IDLH of 500 ppm. Thus, as safety professionals, we will recommend that the tank be opened only under the precautions recommended by NIOSH and OSHA (2016) in their joint hazard alert, *Health and Safety Risks for Workers Involved in Manual Tank Gauging and Sampling at Oil and Gas Extraction Sites*. (In the next issue, Math Toolbox will consider an equation that, coupled with a hydrostatic pressure gauge, can determine the depth of liquid in the tank more safely, without even opening the hatch.)

Notes: The worst-case concentration of vapors in the tank will vary, depending on temperature and pressure (more about this later). Also, be sure to use the same metric for vapor pressure and absolute barometric tank pressure (in this case, we used mm Hg for both). Finally, when looking up vapor pressures, always check the Chemical Abstracts Service (CAS) number to make sure the chemical is correctly identified. In this case, the CAS number for toluol is 108-88-3. It is important to check the consistency of the CAS number on the delivery ticket for the product, on the SDS, on the side of the tank and in the *NIOSH Pocket Guide*.

Alternate example: Let's predict the maximum headspace concentration for a different chemical. Specifically, imagine a tank contains ethyl acetate (CAS 141-78-6) at a temperature of 68 °F (20 °C) and a tank pressure of 760 mm Hg absolute. The SDS indicates that the vapor pressure of ethyl acetate is 73 mm Hg gauge at 68 °F. According to the *NIOSH Pocket Guide*, the IDLH for ethyl acetate is 2,000 ppm. Assuming the vapor concentration has reached equilibrium with the liquid, what is the maximum expected concentration of ethyl acetate vapors in the headspace of the tank (C, in ppm)?

Inserting the known values for vapor pressure of ethyl acetate (73 mm Hg gauge at 68 °F) and absolute barometric pressure inside the tank (760 mm Hg absolute), we solve for maximum headspace vapor concentration (C):

$$C = \frac{73 \cdot 10^6}{760} = 96{,}052.63\ ppm$$

Ethyl acetate has a high vapor pressure, so the predicted worst-case concentration of ethyl acetate vapors within the tank is a whopping 96,052.63 ppm, which far exceeds the IDLH of 2,000 ppm.

You Do the Math

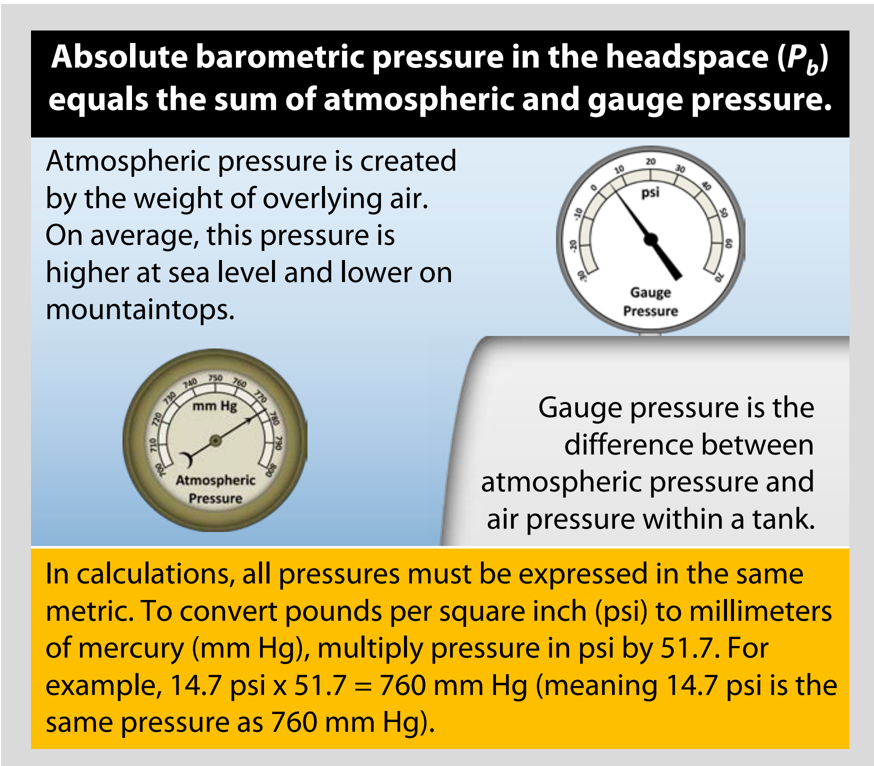
Apply your knowledge to the following question. Answers are on p. 54 of this issue.

1) A tank contains tetrachloroethylene (CAS 127-18-4) at a temperature of 68 °F (20 °C) and a tank pressure of 760 mm Hg absolute. The SDS indicates that the vapor pressure of tetrachloroethylene is 14 mm Hg gauge at 68 °F. The IDLH for tetrachloroethylene is 150 ppm.

a) Assuming the vapor concentration has reached equilibrium with the liquid, what is the maximum expected concentration of tetrachloroethylene vapors in the headspace of the tank (C, in ppm)?

b) Does this concentration exceed tetrachloroethylene's IDLH of 150 ppm?

FIGURE 3
COMPONENTS OF ABSOLUTE PRESSURE



Use the equation:

$$C = \frac{P_v \cdot 10^6}{P_b}$$

What If the Liquid's Temperature Varies?

Sources such as the *NIOSH Pocket Guide* and SDS usually provide vapor pressures for only a few specified temperatures. To predict maximum headspace vapor concentrations under actual field conditions, we must determine vapor pressures for temperatures that exist in the field. We find vapor pressures for varying temperatures using more comprehensive sources such as the National Institute of Standards and Technology (NIST, 2018) Chemistry WebBook.

To illustrate how temperature affects vapor pressures and maximum headspace concentrations, imagine that the tank in the original example now contains toluol at a temperature of 100 °F (37.8 °C) and a tank pressure of 760 mm Hg absolute. The NIST Chemistry WebBook indicates that the vapor pressure of toluol is 53 mm Hg gauge at 100 °F. Assuming the vapor concentration has reached equilibrium with the liquid, what is the maximum expected concentration of vapors in the headspace (C, in ppm) when the temperature of toluol is 100 °F?

Step 1. Start with the equation for headspace saturation vapor concentration:

$$C = \frac{P_v \cdot 10^6}{P_b}$$

where:
C = airborne concentration of vapor in the headspace in ppm
P_v = vapor pressure of the contaminant
P_b = absolute barometric pressure in the headspace

Step 2. Insert the current values for vapor pressure of toluol (53 mm Hg gauge at 100 °F) and absolute barometric pressure inside the tank (760 mm Hg absolute). Then solve for maximum headspace vapor concentration (C):

$$C = \frac{53 \cdot 10^6}{760} = 69{,}736.84\ ppm$$

Step 3. Taking into account the higher toluol temperature of 100 °F, the predicted worst-case concentration of toluol vapors within the tank (69,736.84 ppm) has more than doubled compared to the first example. In general, higher temperatures will result in higher headspace vapor concentrations, while lower temperatures will result in lower concentrations.

Alternate example: Let's predict the maximum headspace concentration for a different chemical. Specifically, imagine a tank contains n-butyl acetate (CAS 123-86-4) at a temperature of 77 °F (25 °C) and a tank pressure of 760 mm Hg absolute. The SDS indicates that the vapor pressure of n-butyl acetate is 11.5 mm Hg gauge at 77 °F. The IDLH for n-butyl acetate is 1,700 ppm. Assuming the vapor concentration has reached equilibrium with the liquid, what is the maximum expected concentration of n-butyl acetate vapors in the headspace of the tank (C, in ppm)?

Inserting the known values for vapor pressure of n-butyl acetate (11.5 mm Hg gauge at 77 °F) and absolute barometric pressure inside the tank (760 mm Hg absolute), we solve for maximum headspace vapor concentration (C):

$$C = \frac{11.5 \cdot 10^6}{760} = 15{,}131.58\ ppm$$

The predicted worst-case concentration of n-butyl acetate vapors within the headspace of the tank is 15,131.58 ppm, which far exceeds n-butyl acetate's IDLH of 1,700 ppm.

You Do the Math

Apply your knowledge to the following question. Answers are on p. 54 of this issue.

2) A tank contains tetrachloroethylene (CAS 127-18-4) at a temperature of 92 °F (33.3 °C) and a tank pressure of 760 mm Hg absolute. The NIST Chemistry WebBook indicates that the vapor pressure of tetrachloroethylene is 28.5 mm Hg gauge at 92 °F. The IDLH for tetrachloroethylene is 150 ppm.

a) Assuming the vapor concentration has reached equilibrium with the liquid, what is the maximum expected concentration of tetrachloroethylene vapors in the headspace of the tank (C, in ppm)?

b) Does this concentration exceed tetrachloroethylene's IDLH of 150 ppm?

Use the equation:

$$C = \frac{P_v \cdot 10^6}{P_b}$$

What If the Barometric Pressure Varies?

The maximum concentration of vapors in the headspace depends in part on the absolute barometric pressure within the tank. To illustrate how barometric pressure affects maximum headspace concentration, imagine the gauge pressure of the toluol tank in the original example is now 20 mm Hg gauge (meaning tank pressure exceeds atmospheric pressure by 20 mm Hg). Also, imagine the atmospheric pressure outside the tank is 750 mm Hg. The resulting absolute barometric pressure is the sum of these two values, as follows: $P_b = 20_{Gauge} + 750_{Atmosphere} =$ 770 mm Hg absolute.

For comparison, let's say the temperature and vapor pressure for toluol remain the same as the original example (68 °F and 21 mm Hg gauge). Assuming the vapor concentration has reached equilibrium with the liquid, what is the maximum expected concentration of toluol vapors in the headspace of the tank (C, in ppm)?

Step 1. Start with the equation for headspace saturation vapor concentration:

$$C = \frac{P_v \cdot 10^6}{P_b}$$

where:

C = airborne concentration of vapor in the headspace, in ppm

P_v = vapor pressure of the contaminant

P_b = absolute barometric pressure in the headspace

Step 2. Insert the known values for vapor pressure of toluol (21 mm Hg gauge at 68 °F) and absolute barometric pressure inside the tank (770 mm Hg absolute). Then solve for maximum headspace vapor concentration (C):

$$C = \frac{21 \cdot 10^6}{770} = 27{,}272.73\ ppm$$

Step 3. Taking into account the higher barometric pressure of 770 mm Hg absolute, the predicted worst-case concentration of toluol vapors within the tank (27,272.73 ppm) is slightly lower than the first example, but still quite hazardous. In general, higher barometric pressures will result in lower headspace vapor concentrations, while lower barometric pressures will result in higher concentrations.

You Do the Math

Apply your knowledge to the following question. Answers are on p. 54 of this issue.

3) A tank contains tetrachloroethylene (CAS 127-18-4) at a temperature of 92 °F (33.3 °C), resulting in a vapor pressure for tetrachloroethylene of 28.5 mm Hg gauge. Imagine the tank's gauge pressure is now less than atmospheric pressure at -24 mm Hg gauge (negative 24) and the atmospheric pressure outside the tank is 770 mm Hg. The absolute barometric pressure is the sum of these two values, as follows: $P_b = (-24_{Gauge}) + 770_{Atmosphere} = 746$ mm Hg absolute.

a) Assuming the vapor concentration has reached equilibrium with the liquid, what is the maximum expected concentration of tetrachloroethylene vapors in the headspace of the tank (C, in ppm)?

b) Does this concentration exceed tetrachloroethylene's IDLH of 150 ppm?

Use the equation:

$$C = \frac{P_v \cdot 10^6}{P_b}$$

How Much Have I Learned?

Try these problems on your own. Answers are on p. 54 of this issue.

4) A tank contains benzene (CAS 71-43-2) at a temperature of 58 °F (14.4 °C). At this temperature, the vapor pressure of benzene is 57 mm Hg gauge. The gauge pressure of the tank is below atmospheric pressure, at -13 mm Hg gauge (negative 13), and the atmospheric pressure outside the tank is 762 mm Hg. Answer the following:

a) What is the absolute barometric pressure in the tank (P_b in mm Hg absolute)?

b) Assuming the vapor concentration has reached equilibrium with the liquid, what is the maximum expected concentration of benzene vapors in the headspace of the tank (C, in ppm)?

c) Does this concentration exceed benzene's IDLH of 500 ppm?

5) A tank contains p-xylene (CAS 106-42-3) at a temperature of 84 °F (28.9 °C). At this temperature, the vapor pressure of p-xylene is 11 mm Hg gauge. The gauge pressure of the tank is above atmospheric pressure, at 9 mm Hg gauge, and the atmospheric pressure outside the tank is 753 mm Hg. Answer the following:

a) What is the absolute barometric pressure in the tank (P_b in mm Hg absolute)?

b) Assuming the vapor concentration has reached equilibrium with the liquid, what is the maximum expected concentration of p-xylene vapors in the headspace of the tank (C, in ppm)?

c) Does this concentration exceed p-xylene's IDLH of 900 ppm?

The Language of Headspace Vapor Science

Readers will encounter the following concepts in codes, certification exams and conversations with other professionals. Match the numbered concepts with their paraphrased definitions (lettered). If you have trouble, you can look up the concepts in resources such as the free online textbook, *College Physics for AP Courses* (see references). Answers are on p. 54 of this issue.

Concepts

6) Absolute barometric pressure
7) Atmospheric pressure
8) Gauge pressure
9) Headspace
10) Vapor
11) Vapor pressure

Definitions (in random order)

a) This is the gaseous state of a substance that is normally a liquid or solid at normal temperature and pressure. It commonly forms by evaporation from a liquid when that liquid is at a temperature lower than its boiling point. It may also form by sublimation of certain solids.

b) This is the pressure exerted by the weight of the overlying air in the atmosphere. At sea level on Earth, this pressure averages about 760 millimeters of mercury (mm Hg), which is approximately 14.7 pounds per square inch (psi), 101 kilopascals (kPa), 1 atmosphere (atm) or 33.9 feet of water column (ft H_2O).

c) The sum of gauge pressure and atmospheric pressure.

d) The space where vapor may form above a liquid in a tank or other closed container.

e) This is a measure of volatility (i.e., the tendency of a liquid to vaporize). In a closed container, it is the pressure of vapor that is in equilibrium with its liquid.

f) The pressure within a closed container (calculated as absolute pressure minus atmospheric pressure). It is positive when it is greater than atmospheric pressure. It is zero when it equals atmospheric pressure. It is negative when it is less than the pressure of the atmosphere.

For Further Study

Learn more from the following source: *ASSP's ASP Examination Prep: Program Review and Exam Preparation*, edited by Joel M. Haight, 2016.

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Establishing a positive safety culture for a company is not easy, especially in the current world economy. Safety professionals need a more practical theory to guide their daily work.

recognizes the huge benefits of a positive safety culture, or when one or few workplaces achieve stage three. At this level, the company starts to facilitate the establishment of a positive safety culture, identifies safety ambassadors (heroes) in other facilities, and establishes a formal program for promoting and supporting safety champions throughout the company. At stage four, safety professionals not only should use the method of walk-the-talk, but also, more importantly, must start applying walk-the-walk principles to facilitate continuous improvement and elevate the quality of the safety culture.

- **Stage 5: Industry level.** At this stage, more and more companies learn from best practices and safety culture becomes a common value for the whole industry. In essence, developing a safety culture becomes an industry standard. At this level, safety becomes a core social value and companies in the same industry begin to support and promote the growth of a safety culture within their own organization. As a result, a beneficial social and industrial transformation is realized. At this matured level, the corporate strategy becomes stalk-the-talk. This involves managers and safety professionals driving continuous improvement by promoting more employee involvement, suggestions and external safety theory. By collecting employee input, we can help facilitate a sustained safety culture.
- **Stage 6: Cross-industry level.** At this highest stage of safety culture development, not only has a single industry recognized the importance of a positive safety culture, but also many other industries have learned the same, and it will finally start to make a difference in our communities, towns, countries and across the globe. At this stage, stalk-the-talk becomes the norm and safety becomes a recognizable part of our karma, or our shared value in treasuring life. We are in this world for a reason. We have families to love, friends to take care of and pals to enjoy working with. Our karma is to treasure the times when we are together.

Both the walk-the-walk and stalk-the-talk methodologies should be employed at higher levels by safety professionals throughout their journey as they develop robust safety cultures. Safety professionals must use these methods when the audience is ready to hear and accept their safety message; they cannot be employed independently without a proper context.

Conclusion

Establishing a positive safety culture for a company is not easy, especially in the current world economy (e.g., tense competition, high turnover rate, labor shortage). Safety professionals need a more practical theory to guide their daily work. By using this theory and method for the past 15 years, the author has successfully established positive safety cultures for three international group companies. The author believes that it can be beneficial for the safety industry. **PSJ**

References

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Math Toolbox, continued from pp. 47-50

Answers: The Case of the Fatal Tank Entry

You Do the Math

Your final digits may be different due to rounding.

1a) $C = \frac{P_v \cdot 10^6}{P_b} = \frac{14 \cdot 10^6}{760} = 18{,}421.05\ ppm$

1b) The maximum expected concentration of 18,421.05 ppm exceeds tetrachloroethylene's IDLH of 150 ppm.

2a) $C = \frac{P_v \cdot 10^6}{P_b} = \frac{28.5 \cdot 10^6}{760} = 37{,}500.00\ ppm$

2b) The maximum expected concentration of 37,500.00 ppm exceeds tetrachloroethylene's IDLH of 150 ppm.

3a) $C = \frac{P_v \cdot 10^6}{P_b} = \frac{28.5 \cdot 10^6}{746} = 38{,}203.75\ ppm$

3b) The maximum expected concentration of 38,203.75 ppm exceeds tetrachloroethylene's IDLH of 150 ppm.

How Much Have I Learned?

Your final digits may be different due to rounding.

4a)

$P_b = P_{Gauge} + P_{Atmosphere} = (-13) + 762 = 749\ mm\ Hg\ absolute$

4b) $C = \frac{P_v \cdot 10^6}{P_b} = \frac{57 \cdot 10^6}{749} = 76{,}101.47\ ppm$

4c) The maximum expected concentration of 76,101.47 ppm exceeds benzene's IDLH of 500 ppm.

5a)

$P_b = P_{Gauge} + P_{Atmosphere} = 9 + 753 = 762\ mm\ Hg\ absolute$

5b) $C = \frac{P_v \cdot 10^6}{P_b} = \frac{11 \cdot 10^6}{762} = 14{,}435.70\ ppm$

5c) The maximum expected concentration of 14,435.70 exceeds p-xylene's IDLH of 900 ppm.

The Language of Headspace Vapor Science

6) c; 7) b; 8) f; 9) d; 10) a; 11) e.