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Gases and Vapors

Patrick N. Breysse, PhD, CIH

Peter S.J. Lees, PhD, CIH

Johns Hopkins University

Section A

Introduction and Definitions

Gases and Vapors

Definition of Gas

- *Gas*—Normal formless state of matter which at room temperature and pressure has low density/viscosity and readily and uniformly distributes itself throughout any container
- Can be organic or inorganic
- Examples: O_2, SO_2, O_3, NO_2, formaldehyde (HCOH), methane (CH_4)

Gases and Vapors

Definition of Vapor

- *Vapor*—Gaseous form of a substance which coexists as a solid or liquid at normal temperature and pressure
- Can be organic or inorganic
- Examples: Hg, H_2O, benzene (C_6H_6), acetone (C_3H_6O), ethanol (C_2H_6O)

Gases and Vapors

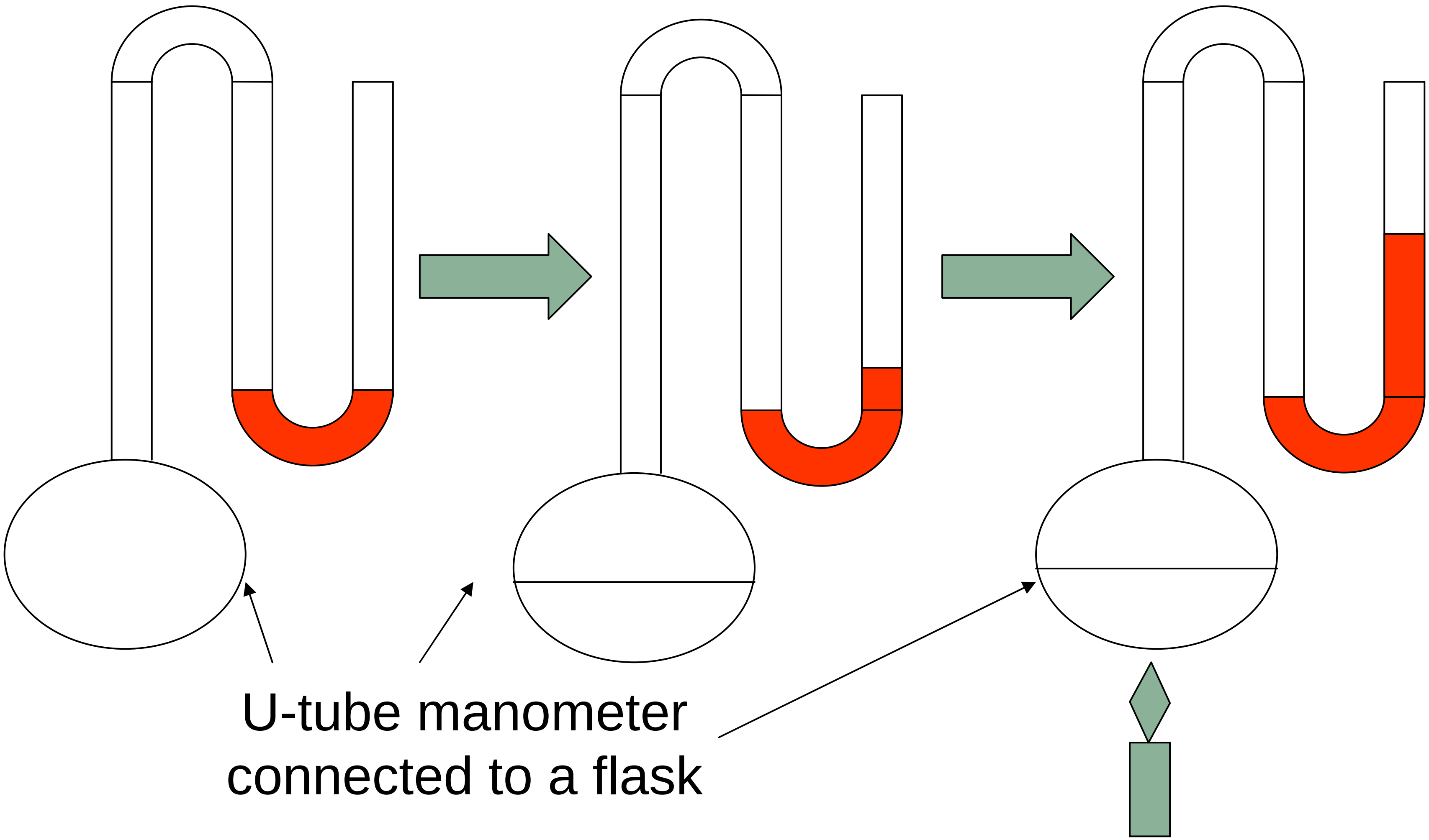
Conditions

- STP (standard temperature and pressure)
  - 0°C and 760 mmHg (32° F and 29.92 inHg; 1 mole of any gas occupies 22.4 liters @ STP)
- NTP (normal temperature and pressure)
  - 25° C & 760 mmHg; 77° F and 29.92 inHg; 1 mole of any gas occupies 24.45 liters @ NTP

Vapor Pressure

- *Vapor pressure* is the pressure exerted when a solid or liquid is at equilibrium with its own vapor; the higher the vapor pressure, the more volatile the chemical
- Vapor pressure is measured in mmHg and is temperature dependent; the higher the temperature, the higher the vapor pressure (and equilibrium concentration)

Measuring Vapor Pressure



Vapor Pressure

- Given two substances of the same volume, which one has more potential hazard?
  - Example: Motor oil vs. ether?
- Ether has more potential hazard than motor oil due to its high vapor pressure and volatility

Health Effects

- Gases and vapors are molecules, and as such, behavior is governed in large part by diffusion
- Exposure (absorption) in respiratory system is largely dependent on gas solubility in mucous membranes
- Gases and vapors can be local irritants or systemic toxins distributed in solution via blood and lymph

Examples of Health Effects

- **Asphyxiants:** Carbon dioxide, carbon monoxide
- **Irritants:** Chlorine, formaldehyde
- **Anesthetics:** Toluene, benzene
- **Hepatotoxins:** Carbon tetrachloride, chlorobenzene
- **Nephrotoxins:** Toluene, xylene

Continued

Examples of Health Effects

- **Neurotoxins:** Carbon disulfide
- **Hematopoietic toxins:** Benzene, carbon monoxide
- **Pulmonary toxins:** Nitrogen dioxide, phosgene
- **Carcinogens:** Benzene, vinyl chloride monomer

Section B

Gas Laws

Boyle's Law

- At constant temperature, the volume (V) occupied by a gas is inversely proportional to the pressure (P); as the pressure goes up, the volume of the gas goes down and vice versa

$$P_1V_1 = P_2V_2 \;\; \& \; \frac{V_1}{V_2} = \frac{P_2}{P_1}; \text{where:}$$

P_1 & V_1 are initial pressure and volume

P_2 & V_2 are final pressure and volume

Continued

Boyle's Law

- Example: If 400 ml of O_2 is collected at 780 mmHg, what volume will the gas occupy if the pressure is changed to 740 mmHg?

$$(780\text{mmHg})(400\text{ml}) = (740\text{mmHg})(X\text{ml})$$

$$X\text{ml} = \frac{(780\text{mmHg})(400\text{ml})}{(740\text{mmHg})}$$

$$X = 422\text{ml}$$

Charles' Law

- At constant pressure, the volume of a gas is directly proportional to its absolute temperature (Kelvin):

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

- Where: T_1 and V_1 = initial temperature and volume, and T_2 and V_2 = final temperature and volume

Continued

Charles' Law

- Example: At a constant pressure, what is the volume of a gas at –20° C if the gas occupied 50 ml @ 0° C?

$$\frac{273\text{K}}{253\text{K}} = \frac{50\,\text{ml}}{\text{X ml}}$$

$$\text{Xml} = \frac{(50\text{ml} \times 253\text{K})}{273\text{K}} = 46.3\text{ml}$$

Boyle's and Charles' Laws Combined

- The density of a gas is related to the volume, temperature, and pressure
- As volume increases, density decreases proportionally; density varies inversely with volume, directly with pressure, and inversely with absolute temperature

Continued

Boyle's and Charles' Laws Combined

- Equations:

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

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

Continued

Boyle's and Charles' Laws Combined

- Example: If a gas occupies 100 ml at 760 mmHg and 27° C, what volume will it occupy at 800 mmHg and 50° C?

$$\frac{(760\text{mmHg})(100\text{ml})}{300\text{K}} = \frac{(800\text{mmHg})(X\text{ml})}{323\text{K}}$$

$$X\text{ml} = \frac{760\text{mmHg} \times 100\text{ml} \times 323\text{K}}{300\text{K} \times 800\text{mmHg}} = 102\text{ml}$$

Ideal Gas Law

$$PV = nRT$$

- P = Pressure (atmospheres)
- V = Volume (liters)
- n = Number of moles of gas (mass in g/molecular weight)
- R = Molar gas constant (0.0821 liter atm/mol K)
- T = Temperature (Kelvin)

Continued

Ideal Gas Law

- Example: What is the volume of 32 g of O_2 at 760 mmHg and 25° C?

$$(1atm)(Xl) = (1mole) * \frac{0.0821latm}{moleK} * 298K$$

$$Xl = (1mole) * \frac{0.0821latm}{moleK} * \frac{298K}{1atm}$$

$$X = 24.45 \text{ liters}$$

Section C

Concentration Units

Gas and Vapor Concentrations

- Concentration equations:

$$C = \frac{\text{mass}_{\text{contaminant}}}{\text{volume}_{\text{air}}} = \frac{\text{volume}_{\text{contaminant}}}{\text{volume}_{\text{air}}} x10^{6}$$

- Concentration units:

  mg/m^3 ppm

Parts Per Million, PPM

- $$\text{ppm} = \frac{\text{parts of contaminant}}{\text{million parts of air}}$$
  - L / 106L or ml / m_3
- Similar to percent

$$\% = \frac{\text{parts}}{100 \text{ parts}}$$

Conversion of Units

- General form of conversion equation

$$Xppm = \frac{Ymg}{m^3} * \frac{mmole}{MW(mg)} * \frac{24.45ml}{mmole}$$

- If X is given, solve for Y, and if Y is given, solve for X
  - Always do a *dimensional analysis* as a check

Continued

Conversion of Units

- Short-hand form of conversion equation:

$$X\,ppm = \frac{Y\,mg}{m^3} * \frac{24.45}{MW}$$

- If X is given, solve for Y, and if Y is given, solve for X

Continued

Conversion of Units

- Example: mg/m^3 to ppm
- Express 50 mg/m^3 benzene in ppm molecular weight of benzene = 78 mg/mmol

$$Xppm = \frac{50mg}{m^3} * \frac{mmole}{78mg} * \frac{24.45ml}{mmol}$$

$$X = 15.7ppm$$

Continued

Conversion of Units

- Example: ppm to mg/m^3
- Express 50 ppm benzene in mg/m^3

$$50ppm = \frac{Ymg}{m^3} * \frac{mmol}{78mg} * \frac{24.45ml}{mmol}$$

$$Y = \frac{159.5mg}{m^3}$$

VP and Concentration

- Calculation of the theoretical "headspace" saturation concentration (worst case)

$$ppm = \frac{VP_{contaminant}(mmHg)}{760mmHg} x10^6$$

Continued

VP and Concentration

- Example: A large storage tank is partially filled with benzene (VP = 82 mmHg at 20° C); what is the theoretical saturation concentration in the headspace above the liquid?

$$ppm = \frac{82mmHg}{760mmHg} x10^{6}$$

$$= 108{,}000 \ ppm$$

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Section D

General Considerations

Benzene Spill Scenario

- A 5 ml vial of benzene was spilled in a 400 m^3 laboratory
- If this were reported to you, the industrial hygienist, how would you respond?
- Assumptions:
  - Room sealed
  - All of the benzene evaporates
  - Lab has well mixed air

Benzene Spill

- PEL for Benzene = 1 ppm (eight-hour TWA)
- Density of benzene = 0.8 g/ml
- MW of benzene = 78 mg/mmol
- Since *concentration = mass/(volume of air),* we need to know what mass of benzene was spilled (i.e., 5 ml = ? g) in order to compare it to the PEL

Continued

Benzene Spill

- Using the density of benzene, we can find the mass of benzene spilled:
  - 5 ml * 0.8 g/ml = 4 g benzene spilled
- Now we can calculate the concentration of benzene using the volume of air in the lab:
  - 4 g benzene / 400 m^3 air = 0.01 g/m^3

Continued

Benzene Spill

- We now have to convert this concentration to ppm, and we start by changing the units to mg/m^3:

$$\left(\frac{0.01\text{g}}{\text{m}^3}\right)\left(\frac{1000\text{mg}}{1\text{g}}\right) = 10\ \frac{\text{mg}}{\text{m}^3}$$

Continued

Benzene Spill

- Now using the molecular weight (78 mg/mmol), we convert to ppm:

$$\left(\frac{10\text{mg}}{\text{m}^3}\right)\left(\frac{\text{mmol}}{78\text{mg}}\right)\left(\frac{24.45\text{ml}}{\text{mmol}}\right) = \frac{3.13\text{ml}}{\text{m}^3}$$

$$3.13\,\frac{\text{ml}}{\text{m}^3} = 3.13\text{ ppm benzene}$$

Continued

Benzene Spill

- 3.13 ppm is 3 times the PEL, but remember that the PEL is a standard designed to protect workers for an eight-hour work day, five times a week, for many years—so don't panic!
- Some recommendations you could make would include closing the lab for a little while and opening a window or turning on or up the ventilation

Benzene Spill Wrap-Up

- The most important point to the benzene spill scenario is that you understand where the numbers (standards and guidelines) come from and how they affect the situation at hand
- Standards and guidelines have purposes, and interpretation of these is essential to good IH decision making

Fire and Explosion Hazards

- *UEL (upper explosive limit)* above which there is insufficient oxygen to cause explosion
- *LEL (lower explosive limit)* below which there is insufficient fuel to cause an explosion
- *Flash point* is the lowest temperature at which a liquid gives off enough vapor to form an ignitable mixture