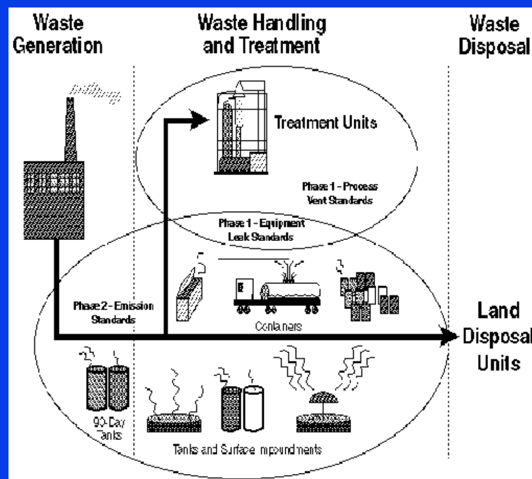
Takin' In Tanks - The Hard Issues of Subpart CC



Subpart CC is Relatively Straightforward ...for a Regulation

- Hazardous waste in a container, tank or surface impoundment?
  - Any exemption?
- VO concentration 500 ppmw or more at point of waste generation, or don’t know VO concentration?
  - Any exclusion?
- Stabilization?
- Container: size and light liquid service?
- Tank: size and vapor pressure?
- Treatment standards, LDRs or NPDES WWTP?

Pumps to move liquids or sludges

Compressors to move air

Pressure relief devices to prevent overstress and blow out or structural failure

Sampling connection systems

Open-ended valves or lines - such as taps, sinks, drains, sumps, ends of transfer lines, chutes. Much more common than often thought.

Valves - gate, ball, swing check, butterfly. May be manual operated or power-assisted.

Flanges and other connectors - joints between pipe lengths or pipes and equipment. May be bolted, slip joint, compression, glued, screwed or welded.

Why do Tanks Become so Hard?

- Vapor pressure determination
- Conservation vents that won't close
- Interaction of Subpart CC and Subpart BB

Also related:

- Inspection access and safety
- Control devices - operation and inspection
- Stabilization requirements
- Record keeping, or lack thereof

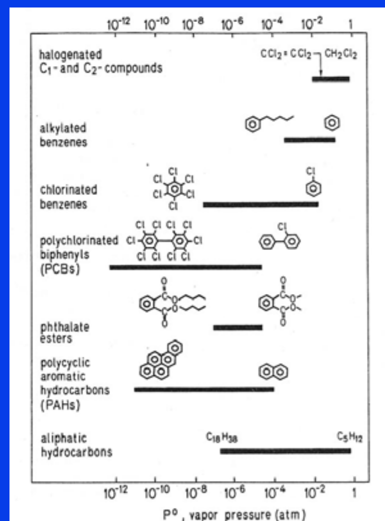
Vapor Pressure Determination

- Regulatory boundary between Level 1 tanks (easy) and Level 2 tanks (control devices and more)
- Determination by analytical method or knowledge of waste
- Without knowledge or determination, facility may need to operate as Level 2 tank
  - $8000 - $10,000 estimated minimum annual cost (based on dedicated carbon recovery system)

Chemistry 101 - What is Vapor Pressure?

- Vapor pressure ($P^{o)}$ is the pressure of the vapor of a compound at equilibrium with its pure condensed phase, be it liquid or solid
- Temperature sets the vapor pressure of a single chemical distributed between two phases
- Most familiar vapor pressure/temperature point is the boiling point of a compound
  - Vapor pressure at T_b = 1 atm (760 mm) (100 kPa)

Vapor Pressure Ranges for Selected Organic Compound Types



Tank Level 1/Level 2 control requirements are based on vapor pressures between 5 x 10^{-2} atm and 7.5 x 10^{-1} atm. While every waste stream should be checked individually, in general the organic compounds that are of most interest to us are:

- •halogenated C_1- and C_2 compounds
- •alkylated benzenes
- •chlorinated benzenes, and
- •aliphatic hydrocarbons

Vapor Pressure Point #1: Vapor Pressure Represents Equilibrium

- At equilibrium, evaporation = condensation
  - Therefore, no more chemical compound can be forced into the gaseous phase
- Agitation won't increase vapor pressure

Vapor Pressure Point #2: Vapor Pressure is a Function of Temperature

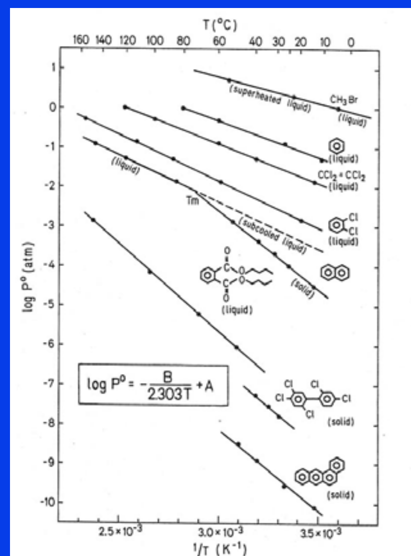
- An increase in temperature causes an increase in the vapor pressure
- Not a linear response but logarithmic (natural log)
- General equations:

  Hexane C_6H_{14} $\ln P^o = 19.19 - 4226 / T(^oK)$

  Dodecane $C_{12}H_{26}$ $\ln P^o = 20.82 - 6825 / T(^oK)$

Vapor pressure is a function of temperature.

Vapor Pressure - Temperature Relationships for Selected Organic Chemicals



For Subpart CC, the vapor pressure range of interest is 5 x 10^{-2} atm to 7.5 x 10^{-1} atm.

What Temperature to Use?

- Subpart CC requires use of average monthly temperature for location of facility
- It is theoretically possible for a specific waste to require a Level 1 tank in October through May but a Level 2 tank in June through September

Vapor Pressure Point #3: Larger Molecules Tend to have Lower Vapor Pressures

- Longer chains create more instantaneous polarity and attraction through van der Waal forces
- Harder to “spring free” from liquid to vapor phase

Vapor Pressure as a Function of n-alkane Molecule Chain Length

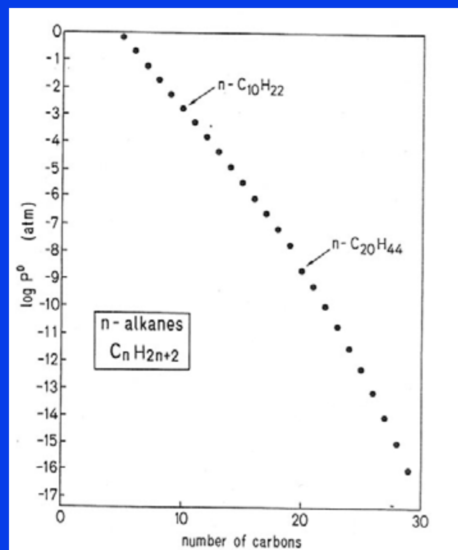


Figure shows aliphatic hydrocarbons with benzene at the top of the line.

Functional Group Effects

TABLE 4.1 Variations in Heats of Vaporization at Normal Boiling Points of Substituted Benzenes

Compound	Substituent(s)	T_b(K)	$\Delta H_{vap}(T_b)$ (kJ·mol^{-1})	μ(D)
Benzene	$-H$	353	30.8	0
Methylbenzene (toluene)	$-CH_3$	384	33.2	0.4
Ethylbenzene	$-CH_2CH_3$	409	35.6	0.6
n-Propylbenzene	$-(CH_2)_2CH_3$	432	38.2	
n-Pentylbenzene	$-(CH_2)_4CH_3$	479	41.2	
n-Heptylbenzene	$-(CH_2)_6CH_3$	519	45.2	
n-Nonylbenzene	$-(CH_2)_8CH_3$	555	49.0	
Isopropylbenzene	$-CH(CH_3)_2$	439	37.5	
Vinylbenzene (styrene)	$-CH=CH_2$	418	37.0	
Fluorobenzene	$-F$	358	31.2	1.57
Chlorobenzene	$-Cl$	405	36.5	1.73
Bromobenzene	$-Br$	429	37.9	1.71
Iodobenzene	$-I$	462	39.5	1.42
1,2-Dichlorobenzene	2 x Cl	454	40.6	2.5
1,4-Dichlorobenzene	2 x Cl	447	39.7	0
Nitrobenzene	$-NO_2$	484	40.8	4.2
Aminobenzene	$-NH_2$	458	44.5	1.5
Hydroxybenzene	$-OH$	455	40.7	1.5
Benzylalcohol	$-CH_2OH$	478	50.6	1.7
Benzoic acid	$-COOH$	522	50.6	

The addition of functional groups results in a reduction of the vapor pressure.

Vapor Pressure Point #4: Wastewater Generally Causes Lower Vapor Pressure

- Humic material and total suspended solids (TSS) tend to combine with organic molecules, creating longer molecules that are harder to volatilize
- However, ionic strength may cause slight increase, as ions impart a tendency of wastewater to repel organic molecules

Experimental Results for Vapor Pressure of Organic Compounds Mixed in Simulated Wastewater

TABLE 2. Henry's Law Constants from Literature and Determined in Pure Water, Wastewater, Experimental Wastewater Simulations, and Calculated[a]

				H_a in simulated wastewater (SD)		
test chemical	lit. H^b	EPICS H (SD)	H_a in wastewater (SD)[c]	humic, 2–150 mg/L	TSS, 100–2500 mg/L	calcd H^d
CH_2Cl_2	0.089	0.105 (0.013)	0.096 (0.02)	0.100 (0.012)	0.081* (0.008)	0.085
$CHCl_3$	0.151	0.166 (0.015)	0.164 (0.013)	0.154 (0.011)	0.147* (0.010)	0.105
TCE	0.396	0.406 (0.021)	0.364* (0.018)	0.366* (0.021)	0.358* (0.020)	0.142
toluene	0.261	0.263 (0.015)	0.221* (0.026)	0.250 (0.016)	0.233* (0.015)	0.115
HMDS	>19	530 (0.3)[e]	64* (57)			na
D5	>19	5.46 (1.02)	0.781* (0.33)			na

[a] An asterisk (*) indicates significantly different from pure water H at 95% CI. na, not available. [b] H of chlorinated chemicals reported by Gossett (*5*), toluene by MacKay (*13*), and silicones by Dow-Corning. [c] $N = 9$ for all except HMDS, where $N = 5$. [d] H calculated (vapor pressure/solubility). [e] Standard error of regression line reported rather than SD.

Conservation Vents

- Conservation vents are pressure operated valves that allow relief from excess pressure or vacuum from the headspace
- Required to prevent structural damage to tanks, particularly from vacuum
- Called conservation vents because designed to "conserve" contents by reducing evaporative losses

For additional information regarding conservation vents see EPA's *Guidance for RCRA Hazardous Waste Air Emission Standards Under 40 CFR Parts 264 and 265*, October 30, 2000.

Two Types of Material Losses for Tanks

- Breathing losses - caused by daily temperature changes and the resulting pressure changes
  - Headspace vapor released when temperature in tank increases and causes pressure increase
  - Atmospheric air brought in when temperature in tank decreases and and causes pressure decrease
- Working losses - caused by headspace volume reduction from increase in tank liquid contents during filling

Potential Amount of Losses - Breathing Losses Example

- Assuming an ideal gas, PV=nRT
  - 20,000 gal tank of which 12,000 gal is headspace
  - Temperature of liquid is constant at 60 ^oF, so no change in vapor pressure
  - Headspace temperature change of 24 ^oF
  - Assume a conservation vent keeps headspace pressure constant at P^o
- Hexane (P^o=12.6 kPa) - 908 kg lost to atmosphere
- Dodecane (P^o=0.008 kPa) - 0.6 kg lost to atmosphere

Potential Amount of Losses - Working Losses

- Assuming an ideal gas, PV=nRT
  - 20,000 gal tank of which 12,000 gal is headspace
  - Tank fills to full, headspace of 2000 gal
  - Assume a conservation vent keeps headspace pressure constant at P^o
- Hexane (P^o=12.6 kPa) - 17,000 kg lost to atmosphere at 60 ^oF
- Dodecane (P^o=0.008 kPa) - 11 kg lost to atmosphere at 60 ^oF

Subpart CC Requirements for Level 1 Tank Conservation Vents

- Level 1: Fixed roof openings can be equipped with
  - Closure devices **<u>if</u>** designed with no visible cracks, holes, gaps or other open spaces when secured in closed position
  - Permanent openings **<u>if</u>** vented to an organic emission control device
  - Pressure relief devices (e.g., conservation vent) that are vented to atmosphere

Subpart CC Requirements for Level 2 Tank Conservation Vents

- If system does not operate under negative pressure (cover vented to a control device):
  - Cover designed to operate with no detectable organic emissions when all cover closure devices are secured in a closed, sealed position, monitored annually
  - Method 21 and less than 500 ppmw above background

Interaction of Subpart CC and Subpart BB

- Subpart CC: tanks with hazardous waste volatile organic concentration in the fluid/solid > 500 ppmw
- Subpart BB: equipment with hazardous waste organic concentration > 100,000 ppmw, including pumps, piping, pressure relief devices and valves
- *Could tank headspace fill with organic vapors at Subpart BB concentrations?*
  - Yes but unlikely unless atmospheric air evacuated

Summary - What Makes Tanks so Hard?

- Vapor pressure determination
- Conservation vents that won't close
- Interaction of Subpart CC and Subpart BB

References

- Schwarzenbach, R. P., Gschwend, P. M., and Imboden, D. M. (1993). Environmental Organic Chemistry, John Wiley & Sons, Inc., New York.

- David, M. D., Fendinger, N. J., and Hand, V. C. (2000). "Determination of Henry's Law Constants for Organosilicones in Actual and Simulated Wastewater", Environmental Science & Technology, Vol. 34, No. 21, pp. 4554-4559.