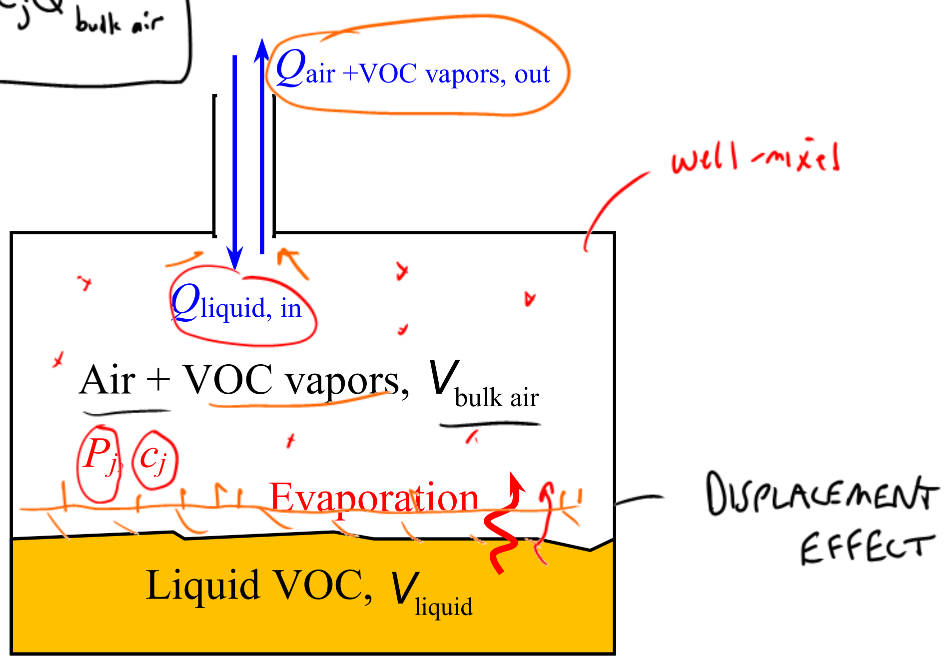
Today, we will:

- Discuss **Tank Filling**, and how to estimate **Vapor Emissions** from filling a tank
- Do an example problem

Emissions from Tank Filling:

Tank Filling – consider filling a tank with some liquid volatile organic compound (VOC):

$$S_j = \dot{m}_j = c_j Q_{\text{bulk air}}$$ ☆



- Cons of mass

$$Q_{\text{bulk air out}} = Q_{\text{liq. in}}$$

- mass conc

$$c_j = \frac{m_j}{\forall_{\text{bulk air}}} = \frac{n_j M_j}{\forall_{\text{bulk air}}}$$

- ideal gas

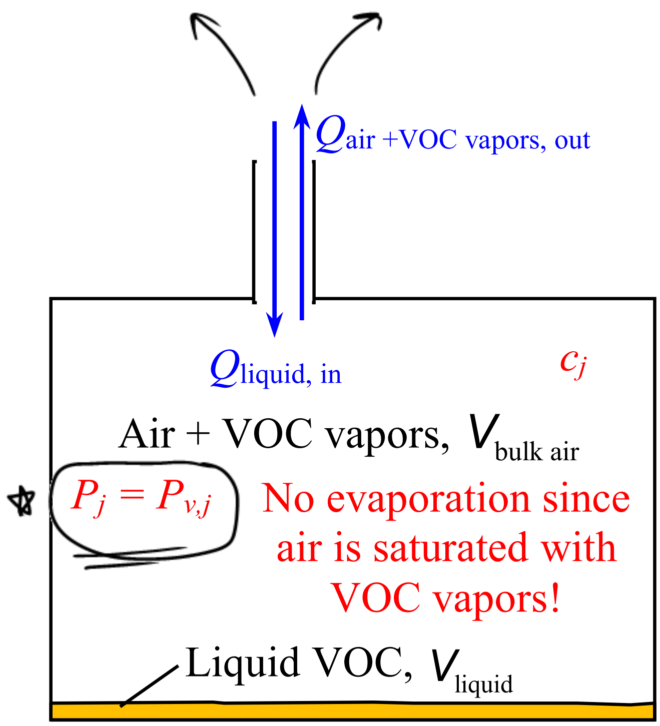
$$P_j \forall_{\text{bulk air}} = n_j R_u T$$

$$c_j = \frac{M_j P_j}{R_u T}$$ ☆

- $\dot{m}_j = S_j = c_j Q_{\text{bulk air}} \rightarrow$

$$\dot{m}_j = \frac{M_j P_j}{R_u T} Q_{\text{liq. in}} \quad ☆☆ \qquad (1)$$

Tank Filling (continued) – consider filling a tank with some liquid volatile organic compound (VOC) for the case in which ***a small amount of the VOC has been sitting in the tank for a long time*** (e.g., filling a nearly empty gas tank in your car):



Ⓠ How much of the VOC vapor is emitted into the air if we fill up the tank with liquid VOC?

Ⓐ <u>ALL OF IT!</u>

(smell).

Example: Emissions from filling your car's gasoline tank

Given: You need gasoline in your car. The tank is nearly empty, but there is still a small amount of liquid gasoline at the bottom of the tank. The tank volume is 15 gallons.

To do: Estimate (to 2 digits) the mass of gasoline vapors emitted into the atmosphere during one fill-up at the gas station.

Solution: First look up the molecular weight and vapor pressure of gasoline at SATP conditions:

- Average molecular weight is M_j = 110 kg/kmol
- Average vapor pressure is $P_{v,j}$ = 169 mm Hg = 22.5 kPa

Use the equation we derived for filling up a tank – displacement vapors are emitted in the bulk air that must come out of the tank as we add liquid (the liquid pushes the bulk air out),

In terms of mass and volume flow rates: $\dot{m}_{j,\text{ displaced}} = \frac{M_j P_j}{R_u T} Q_{\text{liquid in}}$. rate

In terms of mass and volume (not rates): $m_{j,\text{ displaced}} = \frac{M_j P_j}{R_u T} V_{\text{liquid in}}$. mass

Key: Here, since liquid gasoline has been sitting in the tank for a long time, ***the partial pressure of the gasoline vapors is equal to the vapor pressure of the gasoline***.

So, we set $P_j = P_{v,j}$ and plug our numbers into the second equation above,

$$m_{j,\text{ displaced}} = \frac{M_j P_j}{R_u T} V_{\text{liquid in}}$$

$$= \frac{\left(110 \frac{\text{kg}}{\text{kmol}}\right)(22.5 \text{ kPa})}{\left(8.314 \frac{\text{kJ}}{\text{kmol}\cdot\text{K}}\right)(298.15 \text{ K})}(15 \text{ gal})\left(\frac{\text{kJ}}{\text{kN}\cdot\text{m}}\right)\left(\frac{\text{kN}}{\text{m}^2\cdot\text{kPa}}\right)\left(\frac{1 \text{ m}^3}{264.17 \text{ gal}}\right) = 0.057 \text{ kg}$$

Result: We estimated that approximately **0.057 kg** of gasoline vapors are emitted into the atmosphere for each 15-gallon fill-up of gasoline at a gas station.

Quick comment about bias in the media: Which sounds more alarming to the average person on the street?

1. You emit only 0.057 kg of gasoline vapors into the atmosphere by flling up your car.
2. You emit 57 g of gasoline vapors into the atmosphere every time you fill up your car.
3. You emit 57,000 mg of gasoline vapors into the atmosphere every time you fill up your car.
4. *You* pollute and contaminate the air that we all have to breathe by emitting **57,000 mg** of *toxic* and *odorous* gasoline vapors into the atmosphere *each and every* time you fill up *your* car!

Question: How much does this lost gasoline vapor emission cost per fill-up?

Gas price record every Janurary or February since I have taught ME 433:

Updated Table as of January 2025:

Year	Gasoline cost per gallon
2014	$3.50
2015	$2.50
2016	$2.00
2017	$2.50
2018	$2.90
2019	$2.60
2020	$2.60
2021	$2.80
2022	$3.70
2023	$3.80
2024	$3.30
2025	$3.50

Solution:

- From above, we calculated $m_{j,\text{emitted}} = 0.057$ kg
- Gasoline cost = $3.50/gallon
- Look up specific gravity of liquid gasoline: $SG_{\text{gasoline}} = 0.75$
- So, the *density* of the gasoline is $\rho_{\text{gasoline}} = SG_{\text{gasoline}}\rho_{\text{water}} = (0.75)\left(1000\ \frac{\text{kg}}{\text{m}^3}\right) = 750\ \frac{\text{kg}}{\text{m}^3}$
- Conversion: 1 m^3 = 264.17 gallons

Now we can calculate the money (in cents) wasted (lost as vapor into the atmosphere) each time we fill up our gas tank with gasoline:

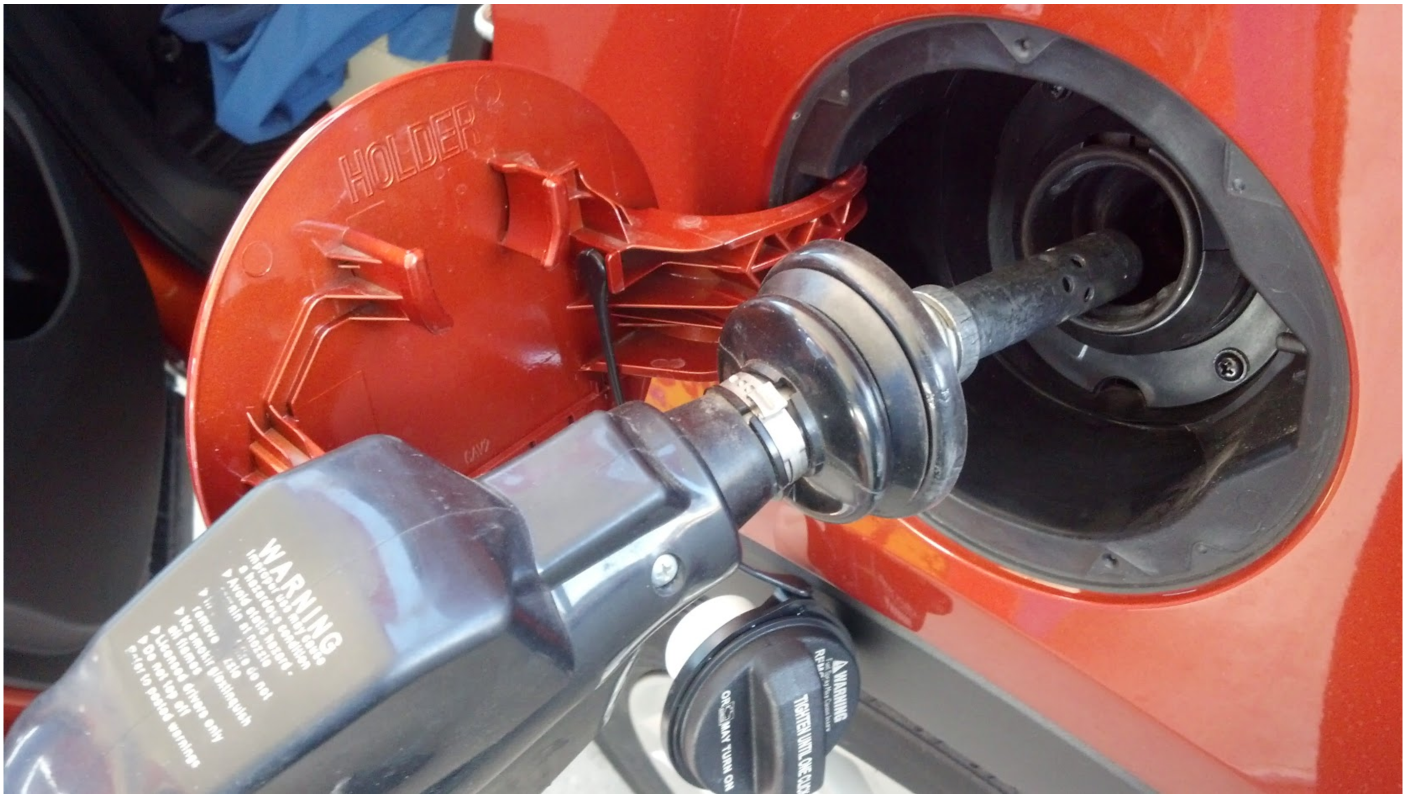
Need to generate an eq. based on units & common sense

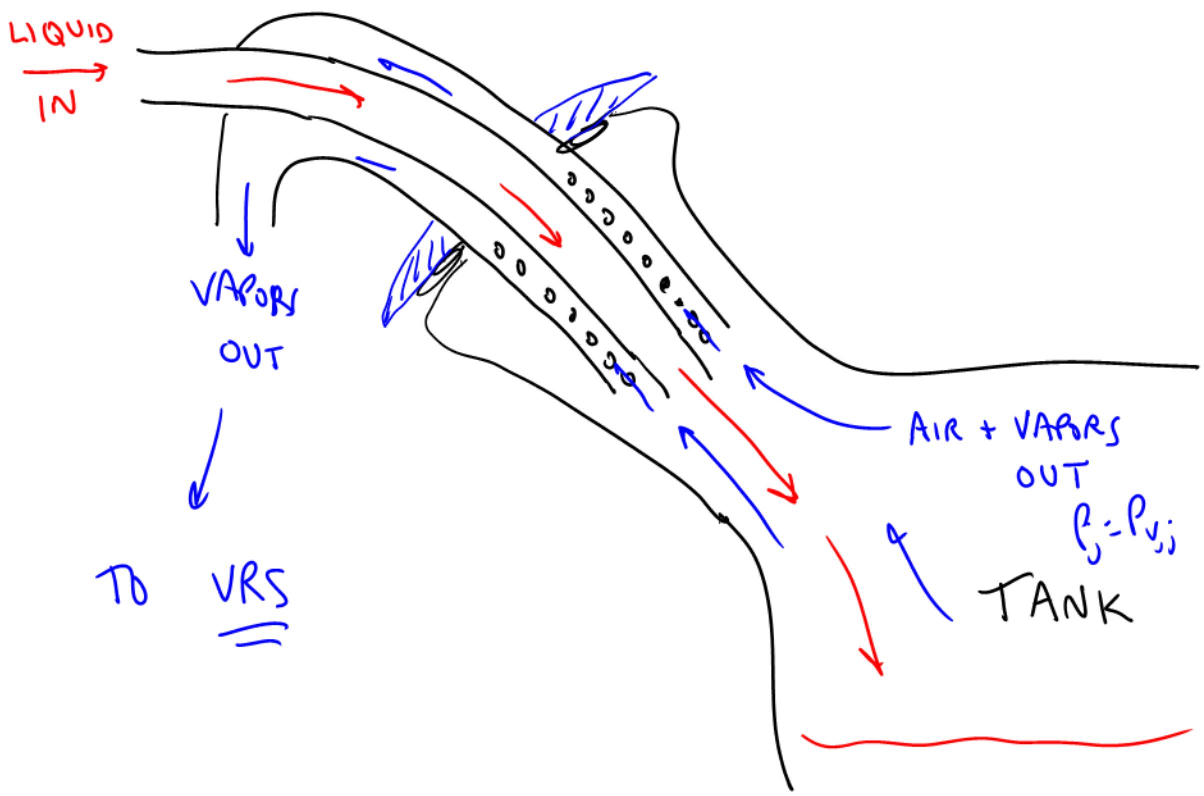
EQ: $$\text{Cost} = \frac{\$3.50}{\text{gal}}\left(0.057\ \text{kg}\right)\left(\frac{\text{m}^3}{750\ \text{kg}}\right)\left(\frac{264.17\ \text{gal}}{\text{m}^3}\right)\left(\frac{100\ \text{cents}}{\$}\right) = 7.0\ \text{cents}$$

THIS IS WASTING MONEY
AND EMITTING AIR POLLUTION

Not possible to eliminate this waste and air pollution unless you have some kind of vapor recovery system

Vapor Recovery System at a gas station:





Other than a sophisticated vapor recovery system, is there any way to avoid these emissions?

Let's define a **filling factor**, f, as follows:

$$f = \frac{\text{Actual partial pressure of } j}{\text{Maximum possible partial pressure of } j} = \frac{P_j}{P_{v,j}}$$

, and $0 < f < 1$.

$f \to 0$ if • empty tank @ t=0 • slow evap. VOC

if tank partially filled

Note that $f = \frac{P_j}{P_{v,j}}$ is kind of like relative humidity, but with some species other than water.

If any amount of VOC has been sitting at the bottom of the tank for a long time, the partial pressure will equal the vapor pressure (the tank is saturated with the VOC vapors), and for this case $f = 1$.

We modify our Equation (1) for the source strength of the emissions:

$$S_j = \dot{m}_{j,\text{ displaced}} = \frac{M_j f P_{v,j}}{R_u T} Q_{\text{liquid in}} \quad \text{where } f = \frac{P_j}{P_{v,j}}$$

For an empty tank initially → f depends on

- How fast the VOC evaporates
- How fast the tank is filled
- How the tank is filled

$0 < f < 1$

Filling Factors for Filling an EMPTY Tank:

(a) Splash Filling

$P_j \approx P_{v,j}$

$f \approx 1$

(b) Submerged Filling

$P_j < P_{v,j}$

$f \approx 0.5$

(c) Bottom Filling

$P_j < P_{v,j}$

$f \approx 0.5$

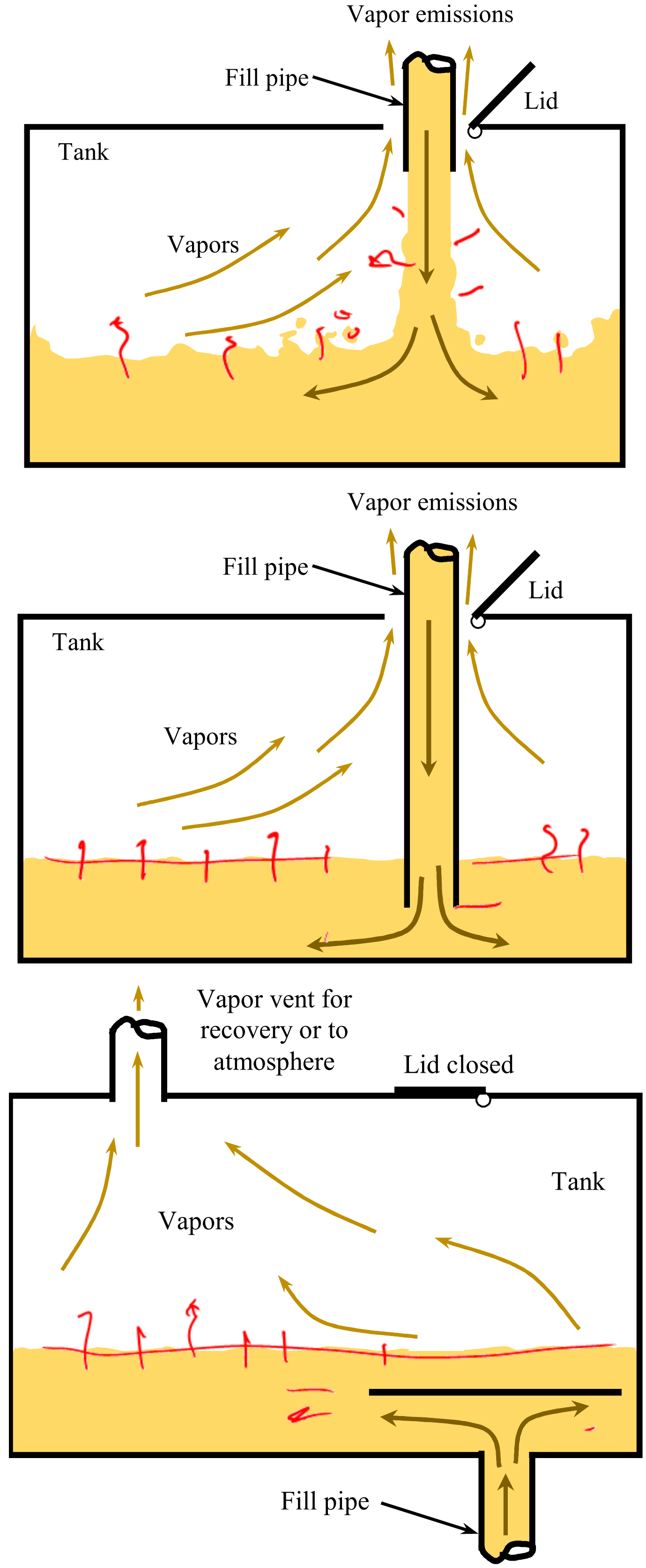


Figure 4.3 Methods to fill vessels with liquids; (a) splash filling, (b) submerged filling, and (c) bottom filling (redrawn from AWMA Handbook on Air Pollution Control, 2000).