

1. The **relative humidity** mentioned in weather reports is defined as $(p_{\text{H}_2\text{O}}/p_{\text{H}_2\text{O}}^*) \times (100 \%)$, where $p_{\text{H}_2\text{O}}$ is the partial pressure of water vapor and $p_{\text{H}_2\text{O}}^*$ is the vapor pressure of pure liquid water.
[3]
How many grams of water vapor are in 1.00 L of moist air at 25 °C and 1.00 bar if the relative humidity is 96 %? (The vapor pressure of pure water at 25 °C is 23.75 mm Hg.)

2. Use the plot of the compression factor against pressure for methane provided in the course notes (and copied overleaf) to answer this question.
[6]
 - a) Calculate the density of methane (in grams per cm³) at 25 °C and 1000 bar.
 - b) Re-calculate the density of methane at 25 °C and 1000 bar assuming ideal-gas behavior. Do attractive methane intermolecular forces dominate under these conditions?
 - c) $Z = 1$ for an ideal gas. From the plot of the compression factor for methane, $Z = 1$ at -100 °C and 270 bar. Is methane an ideal gas under these conditions? Explain.
 - d) Describe an important industrial application that requires accurate compression-factor data for methane.

3. A steel tank (internal volume 50.0 L) is filled with O₂ gas to a pressure of 200 bar at 300 K. Calculate the mass of O₂ in the tank:
[6]
 - a) assuming ideal-gas behavior
 - b) using the van der Waals equation with $a = 1.382 \text{ L}^2 \text{ bar mol}^{-2}$ and $b = 0.0319 \text{ L mol}^{-1}$.
 - c) Which answer, a or b, is likely to be more accurate? Explain.

4. Why is it unreliable to use the ideal gas equation, the van der Waals equation, or any other gas equation of state to estimate the amount of propane in a gas-barbecue tank?
[1]

5.
 - a) Show $(\partial U/\partial V)_T = 0$ for an ideal gas.
 - b) Is $(\partial U/\partial V)_T$ an intensive property (depends on the size of systems) or an extensive property (size-independent)? Justify your answer.
[4]

1. partial pressure of water vapor:

$$P_{H_2O} = \frac{\% RH}{100\%} P_{H_2O}^*$$

$$= 0.96 (23.75 \text{ mm Hg})$$

$$= 22.80 \text{ mm Hg} \times \frac{1}{750.06 \text{ mm Hg bar}^{-1}}$$

$$= 0.0304 \text{ bar}$$

in 1.00 L of moist air:

$$n_{H_2O} = \frac{P_{H_2O} V}{RT}$$

don't use 1.00 bar!
(total pressure)

$$= \frac{(0.0304 \text{ bar})(1.00 \text{ L})}{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}$$

$$= 0.00123 \text{ mol}$$

$$\text{grams of water} = (0.00123 \text{ mol}) \left(\frac{18.01 \text{ g}}{\text{mol}} \right)$$

$$= \boxed{0.0221 \text{ g}} \quad \boxed{22.1 \text{ mg}}$$

conversion factors:

$$\left[1 \text{ mm Hg} = 1 \text{ Torr} = \frac{1}{760.00} \text{ atm} = \frac{1}{750.06} \text{ bar} \right]$$

2. a) at 25 °C and 1000 bar, read from plot =

$$z = 2.02 = \frac{pV_m}{RT}$$

$$V_m = \frac{RT}{p} z = \frac{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) 2.02}{1000 \text{ bar}}$$

$$V_m = 0.0501 \frac{\text{L}}{\text{mol}}$$

$$\text{density} = \frac{\text{molar mass}}{\text{molar volume}} = \frac{16.04 \text{ g mol}^{-1}}{0.0501 \text{ L mol}^{-1}} = \boxed{320. \frac{\text{g}}{\text{L}}}$$

real

b) $V_m = \frac{RT}{p} = \frac{0.08314 (298.15)}{1000} = 0.0248 \frac{\text{L}}{\text{mol}}$
(ideal)

$$\text{density} = \frac{16.04 \text{ g mol}^{-1}}{0.0248 \text{ L mol}^{-1}} = \boxed{647. \frac{\text{g}}{\text{L}}}$$

ideal

$$z = \frac{p}{p_{\text{ideal}}} = 2.02 > 1.00$$

$p > p_{\text{ideal}}$ repulsive forces dominate
(less than) (high pressure)
1000 bar

(also, real density < ideal density)
molecules are pushing each other apart

also: c) methane is not an ideal gas at 270 bar, -100 °C
no gas is ideal attractive and repulsive forces balance and cancel,
at 270 bar but are not zero at 270 bar, -100 °C:

high $z < 1$ at lower pressures, $z > 1$ at higher pressures
but $z = 1$ at all pressures for ideal gases

d) pumping and processing natural gas (mostly methane)

3.

a) O_2 ideal gas

$$V = 50.0 \text{ L}$$
$$p = 200. \text{ bar}$$
$$T = 300 \text{ K}$$

$$pV_m = RT$$

$$V_m = \frac{RT}{p} = \frac{0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1} (300 \text{ K})}{200. \text{ bar}}$$

$$V_m = 0.1247 \text{ L mol}^{-1} = V/n$$

$$n = V/V_m = (50.0 \text{ L}) / (0.1247 \text{ L mol}^{-1})$$
$$= 401. \text{ mol}$$

$$\text{mass } O_2 = (401. \text{ mol}) (32.00 \text{ g mol}^{-1}) = 12,830 \text{ g}$$
$$= \boxed{12.8 \text{ kg}}$$

b) O_2 van der Waals equation

$$V = 50.0 \text{ L}$$
$$p = 200. \text{ bar}$$
$$T = 300 \text{ K}$$

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

solve for V_m

problem!

The van der Waals equation is a cubic in V_m :

$$p(V_m - b)V_m^2 = RTV_m^2 - a(V_m - b)$$

\downarrow
(term in V_m^3)

one method of solving for V_m :

try different trial values of V_m , adjusted to give $p = 200. \text{ bar}$

$$a = 1.382 \text{ L}^2 \text{ bar mol}^{-2} \quad b = 0.0319 \text{ L mol}^{-1}$$

(Table 7.4)

(3. b) cont. try $V_m = 0.1247 \text{ L mol}^{-1}$ (from part a)

1st "guess"

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} = \frac{(0.08314)(300)}{0.1247 - 0.0319} - \frac{1.382}{(0.1247)^2}$$

$$= 268.77 - 88.87$$

$$p = 179.90 \text{ bar} \quad (< 200. \text{ bar})$$

calculated pressure is too low, by about 10%

try a 10% smaller molar volume = $V_m = 0.90(0.1247)$
 $V_m = 0.1122$
 → to increase p
 2nd "guess"

$$p = \frac{(0.08314)(300)}{0.1122 - 0.0319} - \frac{1.382}{(0.1122)^2} = 310.61 - 109.78$$

$$= 200.83 \text{ bar} \quad \text{very close! only } 0.42\% \text{ too high}$$

try a 0.42% larger molar volume = $V_m = 1.0042(0.1122)$
 $V_m = 0.1127$
 3rd "guess"

$$p = \frac{(0.08314)(300)}{0.1127 - 0.0319} - \frac{1.382}{(0.1127)^2} = 308.69 - 108.81$$

$$p = 199.88 \text{ bar} \quad (\text{close enough to } 200. \text{ bar!})$$

$$n = V/V_m = 50.0/0.1127 = 443.6 \text{ mol}$$

$$\text{mass}_{\text{O}_2} = (443.6)(32.00) = \boxed{13.9 \text{ kg}}$$

grams

③c) cont. 200. bar is a "moderately" high pressure
 → O₂ not expected to be ideal

also, O₂ is not an ideal gas, as indicated by
 the different values of V_m calculated in a) and b),
 at 200.0 bar and 300. K

van der Waals estimate of the mass of O₂
 in the tank is probably more accurate

④ gas-barbecue tanks contain liquid propane in
 equilibrium with propane vapor
 (they "slosh" when shaken)

gas equations of state do not include liquids
 (also: pressure is constant for propane(l) ⇌ propane(g) equilibrium)

⑤ a) ^{thermodynamic} equation of state $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

for an ideal gas $\left(P = \frac{nRT}{V}\right)$:

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left[\frac{\partial P}{\partial T} \right]_V - P = T \left[\frac{\partial \left(\frac{nRT}{V} \right)}{\partial T} \right]_V - P$$

n, R, V
constant
here

$$= T \frac{nR}{V} \left(\frac{\partial T}{\partial T}\right)_V - P = \frac{nRT}{V} - P = P - P = 0$$

b) $\left(\frac{\partial U}{\partial V}\right)_T \sim \frac{\Delta U}{\Delta V}$ (at constant T) = $\frac{\Delta(\text{extensive property})}{\Delta(\text{extensive property})}$

~ intensive

system size
effect cancels

U, V
 extensive

also, $\left(\frac{\partial U}{\partial V}\right)_T$ is a pressure (intensive property)