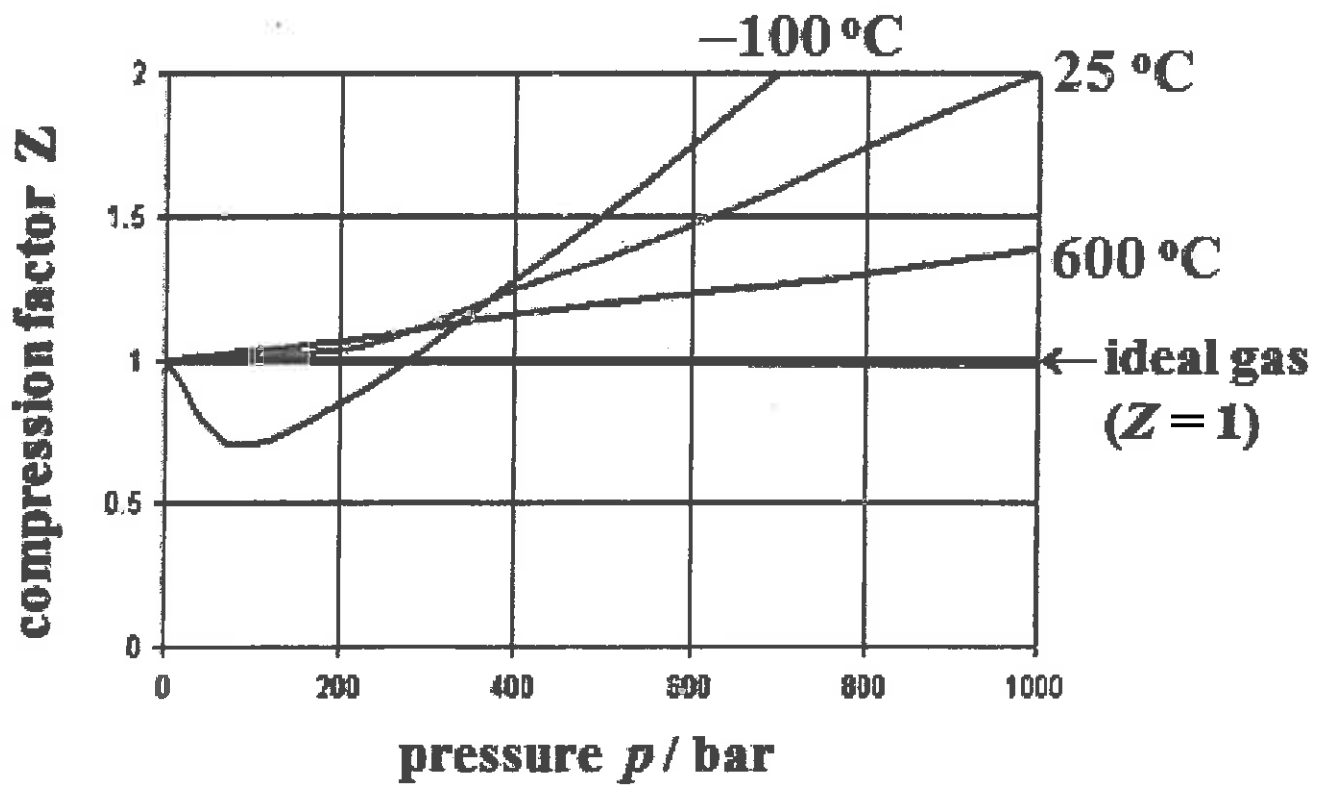


1. Dry air contains N_2 , O_2 , Ar and CO_2 at mole fractions 0.7808, 0.2095, 0.0093 and 0.0004, respectively.
- [6] a) Calculate the partial pressure of oxygen (p_{O_2}) if the total air pressure is 1.000 atm.
- b) Calculate the masses of N_2 , O_2 , Ar and CO_2 in 1.000 L of dry air at 25 °C and 1.000 atm. (The molar masses of N_2 , O_2 , Ar and CO_2 are 28.02, 32.00, 39.95 and 44.01 g mol⁻¹.)
- c) Only trace amounts of CO_2 are present, but CO_2 is a very important constituent of air. Why? Give two reasons.
2. Use the ideal gas law and the plot of the compression factor for methane provided in the course notes (and copied overleaf) to answer this question.
- [6] A tank contains 50.0 L of methane at 25 °C and 400 bar.
- a) Calculate the number of moles of methane in the tank, assuming ideal-gas behavior.
- b) Calculate the number of moles of methane in the tank, using the compression factor, Z .
- c) Which estimate of the number of moles of methane (from part a or from part b) is more reliable? Briefly justify your answer.
- d) Companies such as TransCanada Pipelines consider compression factor data for methane to be of considerable practical importance. Why?
3. If you shake a tank of compressed propane used for a gas barbecue, you can hear “sloshing”.
- [1] How does this “experimental” result prove that propane is not behaving as an ideal gas?
4. To illustrate that a real gas becomes ideal in the limit of zero pressure, show that the van der Waals equation becomes identical to the ideal gas equation as the pressure drops to zero:
- [2]
$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad \rightarrow \quad p = \frac{RT}{V_m} \quad \text{as } p \rightarrow 0$$
5. a) For an ideal gas: $(\partial U/\partial V)_T = 0$. Explain in words why the energy of an ideal gas remains constant if it expands at constant temperature.
- [2] b) For a van der Waals gas: $(\partial U/\partial V)_T = a/V_m^2$. Explain in words why the energy of a van der Waals gas increases if it expands at constant temperature.
6. The density of a sample of ethane (30.07 g mol⁻¹) is 150 g L⁻¹ at 350 K. Calculate the pressure
- [3] a) using the ideal gas law.
- b) using the van der Waals equation ($a = 5.58 \text{ L}^2 \text{ bar mol}^{-2}$, $b = 0.065 \text{ L mol}^{-1}$).

Compression Factor $Z = pV/nRT$ of Methane



1. a) partial pressure of O_2 : $P_{O_2} = x_{O_2} P$

$$x_{O_2} = \text{mole fraction of } O_2 = 0.2095$$

$$P = \text{total pressure} = 1.000 \text{ atm}$$

$$P_{O_2} = (0.2095)(1.000 \text{ atm}) = 0.2095 \text{ atm}$$

b) total number of moles of gas $n = \frac{PV}{RT}$

$$n = \frac{(1.000 \text{ atm})(1.000 \text{ L})}{(0.0820578 \text{ L atm K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}$$

$$n = 0.04087 \text{ mol} = n_{N_2} + n_{O_2} + n_{Ar} + n_{CO_2}$$

$$\text{mass of } N_2 = n_{N_2} M_{N_2} = x_{N_2} n M_{N_2}$$

$$= 0.7807(0.04087 \text{ mol})\left(28.02 \frac{\text{g}}{\text{mol}}\right) = 0.8940 \text{ g}$$

$$\text{mass of } O_2 = 0.2095(0.04087 \text{ mol})\left(32.00 \frac{\text{g}}{\text{mol}}\right) = 0.2740 \text{ g}$$

$$\text{mass of Ar} = 0.0093\left(39.95 \frac{\text{g}}{\text{mol}}\right)(0.04087 \text{ mol}) = 0.0152 \text{ g}$$

$$\text{mass of } CO_2 = 0.0004(0.04087 \text{ mol})\left(44.01 \frac{\text{g}}{\text{mol}}\right) = 0.0007 \text{ g}$$

c) atmospheric CO_2 is i) essential for plant photosynthesis and ii) causes "global warming" (greenhouse gas)

greenhouse gas

CO_2 absorbs infrared radiation

2. a) moles of CH_4 in a 50.0 L tank at 25 °C and 400 bar, assuming it's an ideal gas

$$n = \frac{PV}{RT} = \frac{(400 \text{ bar})(50.0 \text{ L})}{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(25 + 273.15) \text{ K}}$$

$$n = \boxed{806.8 \text{ mol}} (= n_{\text{ideal}})$$

- b) using the compression factor chart

$$z = \frac{PV}{nRT} \Rightarrow n = \frac{1}{z} \frac{PV}{RT} = \frac{n_{\text{ideal}}}{z}$$

read $z = 1.25$ from graph

$$\rightarrow n = \frac{806.8}{1.25} = \boxed{645 \text{ mol}} \quad \text{repulsive forces dominate}$$

- c) answer from b is more reliable — based on experimental data, and CH_4 is not ideal at 400 bar: $z = 1.25$

- d) natural gas — an important fuel and industrial chemical — is mostly methane. z for methane useful for designing high-pressure pumps and pipelines for transporting natural gas through pipelines.

* 645 moles of "real" CH_4 molecules repelling each other exerts the same pressure as 806.8 moles of "ideal" non-interacting CH_4 molecules.

3. "Sloshing" in a tank of compressed propane means liquid propane is present, indicating attractive propane-propane intermolecular forces holding the liquid together \Rightarrow not ideal

4. To show that a van der Waals gas behaves ideally in the limit $p \rightarrow 0$

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad \text{van der Waals equation}$$

rearrange:

$$p = \frac{RT}{V_m} \frac{V_m}{V_m - b} - \frac{RT}{V_m} \frac{a}{RTV_m} \quad \left(\begin{array}{l} \text{note:} \\ \text{common} \\ \text{factor} \\ \frac{RT}{V_m} \end{array} \right)$$

$$p = \frac{RT}{V_m} \left(\frac{V_m}{V_m - b} - \frac{a}{RTV_m} \right)$$

$$p = \frac{RT}{V_m} \left(\frac{1}{1 - \frac{b}{V_m}} - \frac{a}{RT} \frac{1}{V_m} \right)$$

$$\lim_{\substack{V_m \rightarrow \infty \\ (p \rightarrow 0)}} p \rightarrow \frac{RT}{V_m} \left(\underbrace{\frac{1}{1 - \frac{b}{\infty}}}_{\rightarrow 1/(1-0)} - \frac{a}{RT} \underbrace{\frac{1}{\infty}}_{\rightarrow 0} \right)$$

$$= \frac{RT}{V_m} = \text{ideal gas pressure}$$

5. a) ideal gas at constant temperature is expanded: no change in the intermolecular energy because there is no intermolecular energy! (ideal gas)

$$\left(\frac{\partial U}{\partial V} \right)_T = 0$$

b) expand a van der Waals gas at constant T : energy has to be added to the gas to "break" intermolecular attractions, so the energy goes up

$$\left(\frac{\partial U}{\partial V} \right)_T = a/V_m^2 > 0$$

⑥ ethane at 350 K and a density of $150 \frac{\text{g}}{\text{L}}$

$$\text{molar volume } V_m = \frac{V}{n} = \frac{\text{molar mass}}{\text{density}}$$

$$V_m = \frac{30.07 \text{ g mol}^{-1}}{150 \text{ g L}^{-1}} = 0.2005 \frac{\text{L}}{\text{mol}}$$

a) assuming ideal-gas behavior

$$P = \frac{RT}{V_m} = \frac{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(350 \text{ K})}{0.2005 \text{ L mol}^{-1}}$$

$$\boxed{P = 145 \text{ bar}} = P_{\text{ideal}}$$

(143 atm)

b) using the van der Waals equation

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

$$= \frac{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(350 \text{ K})}{(0.2005 - 0.065) \text{ L mol}^{-1}} - \frac{5.58 \text{ L}^2 \text{ bar mol}^{-2}}{(0.2005 \text{ L mol}^{-1})^2}$$

$$= 214.7 \text{ bar} - 138.8 \text{ bar}$$

$$\boxed{P = 75.9 \text{ bar}}$$

(75.0 atm)

notice:

$$Z = \frac{P}{P_{\text{ideal}}} = \frac{75.9 \text{ bar}}{145 \text{ bar}}$$

$$Z = 0.52$$

(strongly nonideal,
attractive forces dominate)