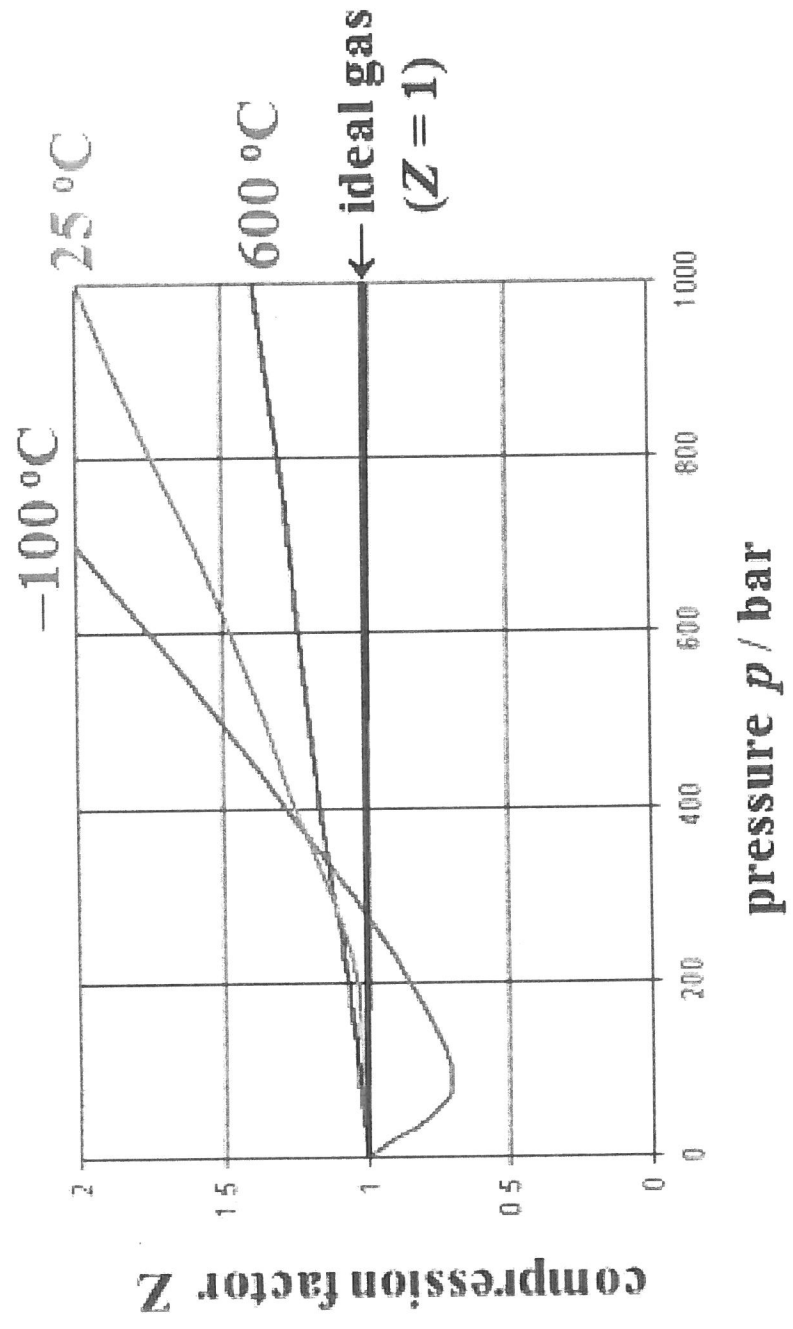


1. A sample of moist air consists of  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$  and Ar at mole fractions 0.790, 0.186, 0.015 and 0.009, respectively, at 1.000 bar total pressure.
- Use the ideal gas law to calculate the partial pressure of oxygen ( $p_{\text{O}_2}$ ).
  - Use the ideal gas law to calculate the mass of water vapor in 1.00 L of the air. Use  $18.02 \text{ g mol}^{-1}$  for the molecular weight of water.
- [5] c) Accurate answers to **a** and **b** can be obtained using the ideal gas equation, ignoring the effects of intermolecular interactions. Why?
2. A tank contains 50.0 L of methane at  $25^\circ\text{C}$  and 800 bar. Calculate the number of moles of methane in the tank using:
- the ideal gas law
  - the van der Waals equation with  $a = 2.28 \text{ bar L}^2 \text{ mol}^{-2}$  and  $b = 0.0427 \text{ L mol}^{-1}$  (*hint: solving the van der Waals equation gives  $V_m = 0.0600 \text{ L mol}^{-1}$* )
  - the graph of the compression factor (next page).
- [7] d) Which estimate of the number of moles of methane (**a**, **b** or **c**) is most reliable? Explain.
3. The graph of the compression factor of methane plotted on the next page shows that  $Z = 1$  at  $-100^\circ\text{C}$  and 280 bar. Is the gas ideal at this temperature and pressure? Justify your answer.
- [2]
4. a) Any real gas becomes ideal in the limit of zero pressure (infinite molar volume). To illustrate this behavior, use the virial equation
- $$Z = \frac{pV_m}{RT} = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \dots$$
- [3] to show  $p \rightarrow RT/V_m$  as  $V_m \rightarrow \infty$ .
- b) The equation of state  $p = \frac{RT}{V_m - b} - \frac{d}{V_m}$  with constants  $b$  and  $d$  is unacceptable. Why?
5. a) For an ideal gas, use the thermodynamic equation of state to show  $(\partial U/\partial V)_T = 0$ .
- [3] b) Is  $(\partial U/\partial V)_T$  an intensive property or an extensive property? Explain. (... page 2)

Compression Factor  $Z = pV/nRT$  of Methane



$$\textcircled{Q1} \text{ a) } \frac{\text{partial pressure of } O_2}{\text{total pressure}} = \frac{P_{O_2}}{P} = \frac{n_{O_2} \frac{RT}{V}}{n \frac{RT}{V}} = \frac{n_{O_2}}{n}$$

$$\frac{P_{O_2}}{P} = \frac{\text{moles of } O_2}{\text{total moles}} = \frac{n_{O_2}}{n} = \text{mole fraction of } O_2 = x_{O_2}$$

$$P_{O_2} = x_{O_2} P = 0.186 (1.000 \text{ bar}) = \boxed{0.186 \text{ bar}}$$

$$\text{b) } P_{H_2O} = x_{H_2O} P = n_{H_2O} \frac{RT}{V}$$

$$\begin{array}{l} \text{moles of} \\ \text{water vapor} \end{array} \quad n_{H_2O} = x_{H_2O} P \frac{V}{RT}$$

$$n_{H_2O} = 0.015 (1.000 \text{ bar}) \frac{1.00 \text{ L}}{(0.08314 \frac{\text{L bar}}{\text{K mol}}) (300 \text{ K})}$$

$$n_{H_2O} = 6.01 \times 10^{-4} \text{ mol}$$

$$\begin{array}{l} \text{mass of} \\ \text{water} \end{array} = (6.01 \times 10^{-4} \text{ mol}) (18.02 \text{ g mol}^{-1}) = \boxed{0.0108 \text{ g}}$$

c) No need to worry about non-ideal gas effects here!

The pressure is quite low (1.000 bar), so the compression factor is almost 1.000.

(intermolecular forces important at:   
 high pressure   
 low temperature   
 (e.g. liquefaction))

Q2) 50.0 L of methane at 25°C and 800 bar

$$T = 273.15 + 25 = 298.15 \text{ K}$$

a) ideal gas law

number of moles of methane in the tank  $n = \frac{PV}{RT} = n_{\text{ideal}}$

$$n = \frac{(800 \text{ bar})(50.0 \text{ L})}{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = \boxed{1614 \text{ mol}}$$

b) van der Waals equation

$$a = 2.28 \text{ bar L}^2 \text{ mol}^{-2}$$

$$b = 0.0427 \text{ L mol}^{-1}$$

$$T = 298.15 \text{ K}$$

$$P = 800 \text{ bar}$$

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

gives  $V_m = 0.0600 \frac{\text{L}}{\text{mol}} = \frac{V}{n}$

moles of methane  $n = \frac{V}{V_m} = \frac{50.0 \text{ L}}{0.0600 \text{ L mol}^{-1}} = \boxed{833 \text{ mol}}$

c) Compression Factor Diagram

for  $P = 800 \text{ bar}$  at  $25^\circ\text{C}$ , read  $Z = 1.75$  (from diagram) (see graph)

$$Z = \frac{PV}{nRT} \quad n = \frac{1}{Z} \frac{PV}{RT} = \frac{1}{Z} n_{\text{ideal}} = \frac{1614 \text{ mol}}{1.75}$$

$$n = \boxed{922 \text{ mol}}$$

(Q2 cont.)

d) "best" estimate of the number of moles of methane?

c using compression factors from measured values of  $P, V, T, n$

"worst": a using the ideal gas law  
(the gas is strongly nonideal ( $Z = 1.75 \neq 1$ ))

"better" b van der Waals equation allows approximate corrections for nonideal behavior

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(Q3) No way methane can be ideal at 280 bar (a relatively high pressure) and  $-100^\circ\text{C}$  (a relatively low temperature, almost liquefaction due to attractive intermolecular forces)

$Z = 1$  at 280 bar,  $-100^\circ\text{C}$  by "accident":

attractive intermolecular forces cancel repulsive intermolecular forces

for an ideal gas,  $Z = 1$  at all pressures and temperatures, not a single point such as 280 bar,  $-100^\circ\text{C}$

Q4 a) show  $p \rightarrow \frac{RT}{V_m}$  as  $V_m \rightarrow \infty$  for the

virial equation 
$$\frac{pV_m}{RT} = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \dots$$

define  $x \equiv \frac{1}{V_m}$   $x \rightarrow \frac{1}{\infty}$  as  $V_m \rightarrow \infty$

so  $x \rightarrow 0$  as  $V_m \rightarrow \infty$

$$\frac{pV_m}{RT} = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \dots = 1 + xB(T) + x^2C(T) + \dots$$

in the limit  $x \rightarrow 0$   
( $V_m \rightarrow \infty$ ) 
$$\frac{pV_m}{RT} \rightarrow 1 + (0)B(T) + (0)C(T) = 1$$

if  $\frac{pV_m}{RT} = 1$  then  $p = \frac{RT}{V_m}$

b)  $p = \frac{RT}{V_m - b} - \frac{d}{V_m}$  multiply by  $\frac{V_m}{RT}$

$$\frac{pV_m}{RT} = \frac{RT}{V_m - b} \frac{V_m}{RT} - \frac{d}{V_m} \frac{V_m}{RT} = \frac{1}{1 - \frac{b}{V_m}} - \frac{d}{RT}$$

in the limit  $V_m \rightarrow \infty$   
( $\frac{1}{V_m} \rightarrow 0$ )

$$\frac{pV_m}{RT} \rightarrow \frac{1}{1 - \frac{b}{\infty}} - \frac{d}{RT} = 1 - \frac{d}{RT}$$

impossible result!

Z must be 1 as  $V_m \rightarrow \infty$

(Q5)

a) thermodynamic  
equation of state  
for an ideal gas  
( $P = \frac{nRT}{V}$ )

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

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

$$= \frac{nRT}{V} - P = \frac{nRT}{V} - \frac{nRT}{V} = 0$$

b)  $\left(\frac{\partial U}{\partial V}\right)_T$  extensive or intensive?

from the equation  $\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$

notice  $\left(\frac{\partial U}{\partial V}\right)_T$  has the same units  
as the pressure, which is intensive (size independent),  
so  $\left(\frac{\partial U}{\partial V}\right)_T$  is **intensive** too

notice also  $\left(\frac{\partial U}{\partial V}\right)_T \approx \frac{\Delta U}{\Delta V} \left( \text{at const. } T \right) = \frac{\text{extensive property}}{\text{extensive quantity}}$

size effects for U and V cancel,

making  $\left(\frac{\partial U}{\partial V}\right)_T$  **intensive**