Chemistry 231 **Assignment #1** (due Tuesday, 19 September, in class)

1. A 20.0 L tank contains 360 grams of propane (molar mass 44.1 g mol^{-1}) at 25.0 °C.

[6]

a) Use the ideal gas law to calculate the pressure in the tank.

b) Calculate the pressure in the tank using the van der Waals equation ($a = 9.38$ bar L^2 mol^{-2} and $b = 0.0903$ L mol^{-1} for propane).

c) Which pressure calculation, part **a** or part **b**, is more reliable? Justify your answer.

d) Liquid propane at 25.0 °C boils at 9.71 bar. Is any liquid propane in the tank? Explain.

2. [3]

a) For any valid nonideal gas equation of state, why must $p \to RT/V_m$ in the limit $V_m \to \infty$?

b) For the van der Waals equation $\left(p = \dfrac{RT}{V_m - b} - \dfrac{a}{V_m^2}\right)$, prove $p \to RT/V_m$ as $V_m \to \infty$.

3. Use the following data for H_2 at 273.15 K (0.00 °C) to calculate the second virial coefficient $B(T)$ and third virial coefficient $C(T)$ at this temperature. Also, show that the fourth virial coefficient $D(T)$ is negligibly small.

[6]

p / bar	V_m / (L mol^{-1})	$Z = pV_m/RT$	$(Z-1)V_m$
50.7	0.4634	1.0345	0.0160
101.3	0.2386	1.0642	0.0153
202.6	0.1271	1.1338	0.0170
303.9	0.09004	1.2048	0.0184

Suggestion: The virial equation $$Z = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \frac{D(T)}{V_m^3} + \cdots$$

rearranges to give $$(Z - 1)V_m = B(T) + \frac{C(T)}{V_m} + \frac{D(T)}{V_m^2} + \cdots$$

If the fourth virial coefficient $D(T)$ is negligible, then a plot of $(Z-1)V_m$ against $1/V_m$ is a straight line with intercept $B(T)$ and slope $C(T)$.

See Question 10, Tutorial #1.

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4. Xenon is rare and valuable, selling for about CAD $2.50 per gram.

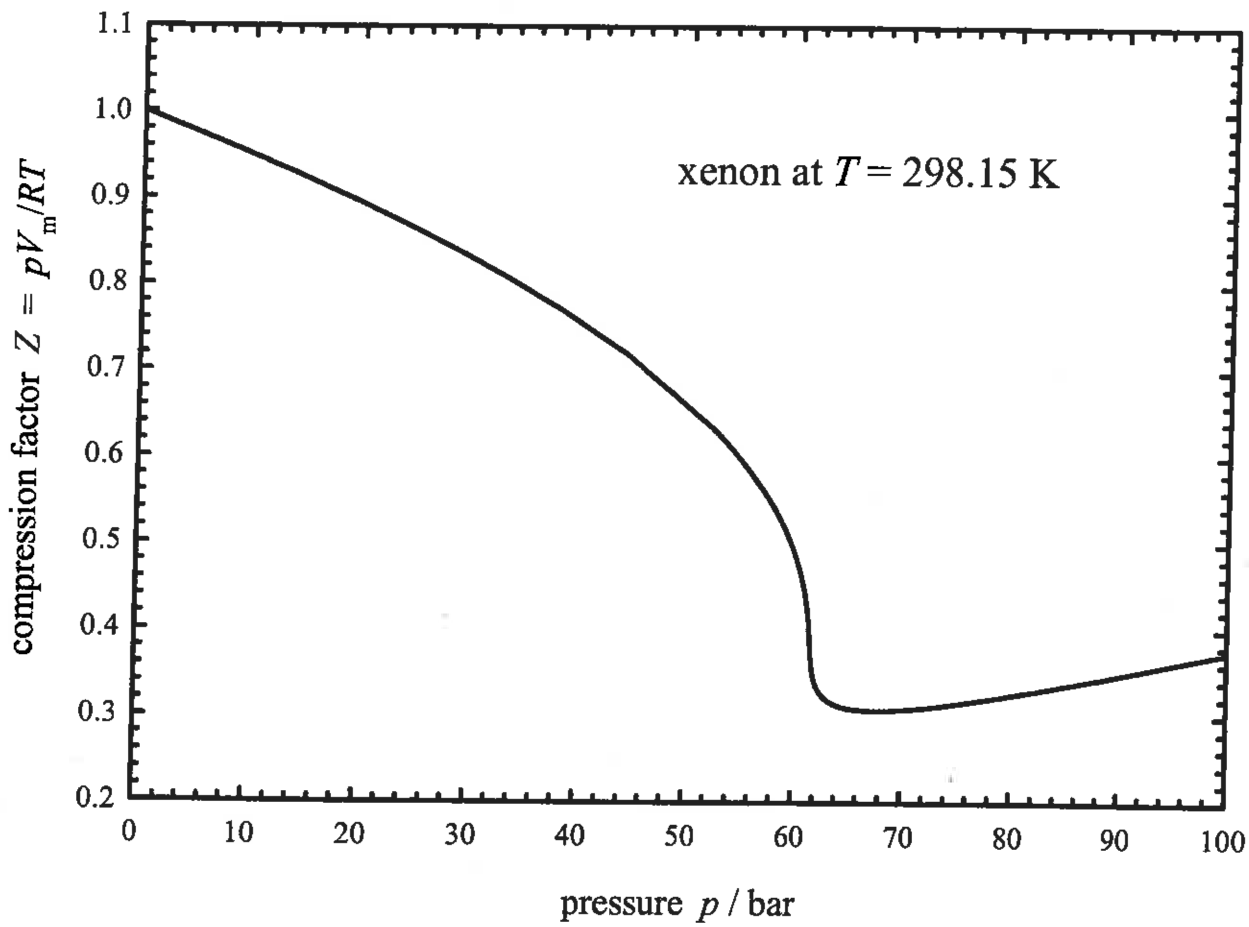
Cleaning out a retired professor's lab, suppose you find a 10.0 L cylinder containing xenon gas. The pressure gauge on the cylinder reads 55.0 bar at 25.0 °C (298.15 K).

[5]

a) Use the ideal gas equation to estimate the dollar value of the xenon in the cylinder.

b) Use the compression factor of xenon at 25.0 °C plotted against the pressure in the diagram below to estimate a more accurate value of the xenon in the cylinder.

c) Do repulsive inter-atomic forces dominate over attractive inter-atomic forces for xenon at 55.0 bar and 25.0 °C. Explain.



Chem 231 <u>Assignment #1</u>

(Q1) 360 grams of propane in a 20.0 L tank:

moles of propane $n = \frac{\text{mass}}{\text{molar mass}} = \frac{360\ g}{44.1\ g\ mol^{-1}} = 8.163\ mol$

molar volume $V_m = \frac{V}{n} = \frac{20.0\ L}{8.163\ mol} = 2.450\ L\ mol^{-1}$

a) <u>ideal gas pressure</u> $p = \frac{nRT}{V} = \frac{RT}{V/n} = \frac{RT}{V_m}$

$$p = \frac{(0.08314\ L\ bar\ K^{-1} mol^{-1})(298.15\ K)}{2.450\ L\ mol^{-1}} = \boxed{10.12\ bar}$$

[$T = (25.0 + 273.15)K = 298.15\ K$]

b) van der Waals pressure

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} = \frac{(0.08314\ L\ bar\ K^{-1} mol^{-1})(298.15\ K)}{(2.450 - 0.0903)\ L\ mol^{-1}} - \frac{9.38\ bar\ L^2 mol^{-2}}{(2.450\ L\ mol^{-1})^2}$$

$p = 10.505\ bar - 1.562\ bar$ $\boxed{p = 8.94\ bar}$

c) $p = 8.94$ bar (part b) probably more reliable because nonideal effects are included, at least approximately

d) <u>liquid probably not present</u>: 8.94 bar is lower than the boiling pressure (9.71 bar) at 25.0 °C

(Q2) a) As the pressure of any gas (real or ideal) drops to zero ($V_m \to \infty$), the molecules become infinitely far apart and do not interact. Result:

All gases become ideal and obey $pV_m = RT$ in the limit $p \to 0$.

b) Prove $p \to \dfrac{RT}{V_m}$ as $V_m \to \infty$

for the van der Waals equation.

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

rearrange to get a common factor of $\dfrac{RT}{V_m - b}$:

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

as $V_m \to \infty$, $\dfrac{V_m}{V_m - b} \to 1$ and $\dfrac{a}{RT}\dfrac{1}{V_m} \to 0$

$$\text{so } \lim_{V_m \to 0} p = \frac{RT}{V_m}(1 - 0) = \frac{RT}{V_m}$$

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recall
<u>l'Hopital's Rule</u>

$$\lim_{V_m \to \infty} \frac{V_m}{V_m - b} = \lim_{V_m \to \infty} \frac{\frac{dV_m}{dV_m}}{\frac{d(V_m - b)}{dV_m}} = \frac{1}{1} = 1$$

(Q2) Virial Equation of state

$$Z = \frac{pV_m}{RT} = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \frac{D(T)}{V_m^3} + \cdots$$

How are virial coefficients $B(T)$, $C(T)$, $D(T)$... evaluated?

Multiply $Z - 1$ by V_m to get

$$\left(Z - 1 = \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \frac{D(T)}{V_m^3} + \cdots \right) V_m$$

$$(Z-1)V_m = B(T) + C(T)\frac{1}{V_m} + D(T)\frac{1}{V_m^3} + \cdots$$

Notice that if $D(T)$ and higher virial coefficients are negligible, then

$$(Z-1)V_m = B(T) + C(T)\frac{1}{V_m}$$

Plot $(Z-1)V_m$ against $\frac{1}{V_m}$ $\Rightarrow$ intercept $B(T)$, slope $C(T)$

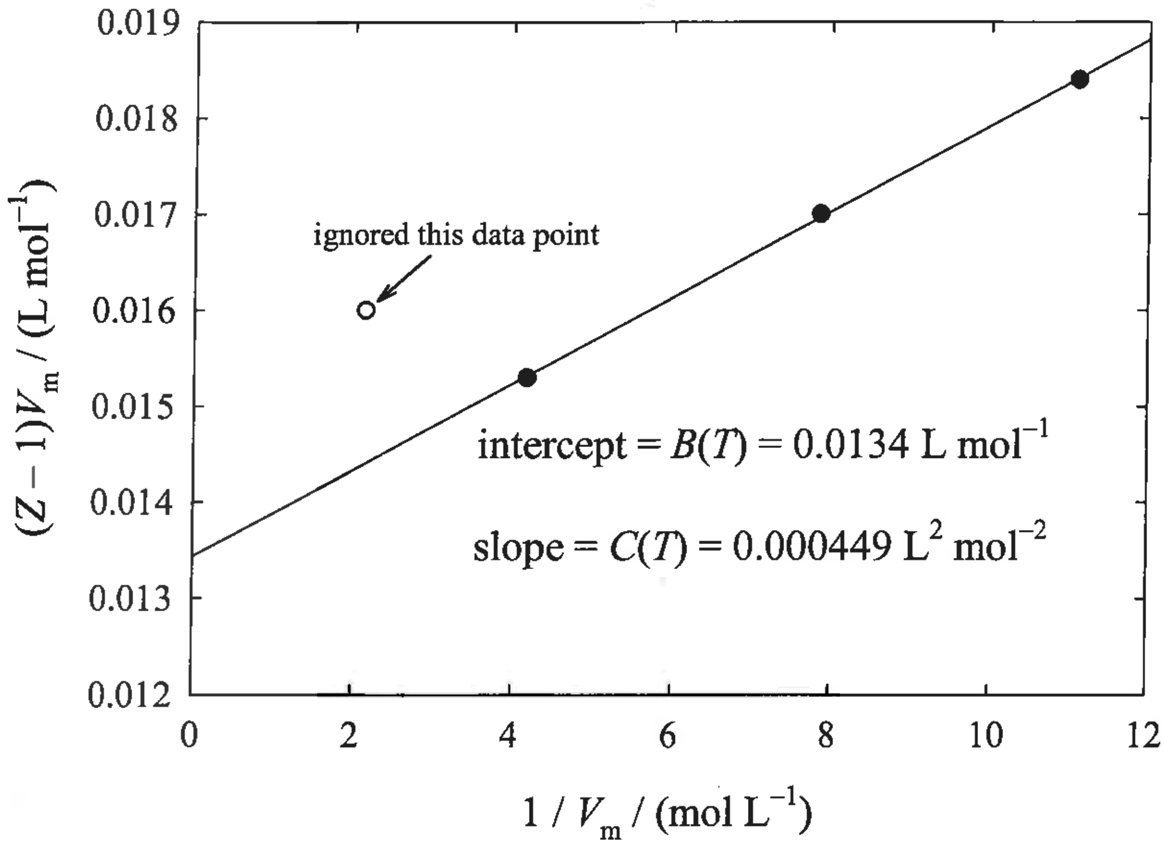
Data provided for H_2 gas at 273.15 K:

$(1/V_m)$ / (mol L^{-1})	$(Z-1)V_m$ / (L mol^{-1})	
2.158*	0.0160*	(at 50.7 bar
4.191	0.0153	101.3 bar
7.868	0.0170	202.6 bar
11.106	0.0184	303.9 bar)

* this data point looks "bad"! (often happens in the real world)

(Q3 cont.)

$(Z-1)V_m$ vs. $1/V_m$ plot for Q3



Q4

a) moles of Xe in the tank using the ideal gas law:

$$n = \frac{pV}{RT} = \frac{(55.0 \text{ bar})(10.0 \text{ L})}{(0.08314 \text{ L bar K}^{-1}\text{ mol}^{-1})(298.15 \text{ K})} = 22.19 \text{ mol}$$

$$\text{Xe mass} = nM = (22.19 \text{ mol})(131.3 \text{ g mol}^{-1}) = 2914 \text{ g}$$

$$\text{Xe value} = (2914 \text{ g})(2.50 \text{ \$ g}^{-1}) \boxed{= \$7,284}$$

b) moles of Xe using the compression factor graph:

at $p = 55.0$ bar, read $Z = 0.60$ from the graph

$$Z = \frac{pV}{nRT} \implies n = \frac{pV}{ZRT} = \frac{1}{Z}\left(\frac{pV}{RT}\right)$$

(get from part a)

$$n = \frac{1}{0.60}(22.19 \text{ mol}) = 36.98 \text{ mol}$$

$$\text{Xe mass} = (36.98 \text{ mol})(131.3 \text{ g mol}^{-1}) = 4856 \text{ g}$$

$$\text{Xe value} = (4856 \text{ g})(2.50 \text{ \$ g}^{-1}) \boxed{= \$12,140}$$

c) $Z = 0.60 < 1$ $\quad p = Z\frac{nRT}{V}$

$p = Z\, p_{\text{ideal gas}}$ $\quad p < p_{\text{ideal gas}}$

attractive forces dominate