Solutions, Problem Set #1
CHM 3400, Fall 2011, Dr. Chatfield

1. The virial equation is a power series, so it can be made as exact as you want by keeping more and more terms (it is "systematically improvable"). However, the parameters B, C, etc. do not have obvious physical interpretations. The van der Waals equation is based on physical reasoning (a accounts for intermolecular forces and b accounts for molecular size). However, because of this, it is not obvious how to add more parameters to increase the accuracy. Finally, the virial equation is applicable to a wider range of temperatures because B, C, etc. are explicitly functions of temperature, whereas a and b are not. It should be noted, though, that obtaining B and C over a wide range of temperatures requires many physical measurements.

2. (Atkins 1.12)

$$\frac{P_1 T_1}{V_1} = \frac{P_2 T_2}{V_2}$$

One must assume pressure is constant to do this problem, i.e. $P_1 = P_2$

$$T_2 = T_1 \frac{V_2}{V_1} \cdot \frac{P_1}{P_2}$$

$$= 295.35\,K \left(\frac{0.100\,K}{1.004}\right) = 29.5\,K$$

3. (Atkins 1.19)

A 1-Liter sample weighs $1.23\,g = 0.00123\,kg$

$$n = \frac{pV}{RT} = \frac{25.5\,kPa \cdot 1\,L}{8.3145\,L\,kPa\,K^{-1}\,mol^{-1} \cdot 330\,K} = 0.00929\,mol$$

$$M = \frac{m}{n} = \frac{0.00123\,kg}{0.00929\,mol} = 0.132\,kg/mol = 132\,g/mol$$

4. (Atkins 1.25)

$$z = \frac{2^{1/2} N_A \sigma c p}{RT} \qquad \sigma(Ar) = 0.36\,nm^2 \quad T = 25^\circ C = 298\,K$$

$$R = 8.31447\ J\,K^{-1}\,mol^{-1}$$

$$N_A = 6.02214\times10^{23}\ mol^{-1}$$

We still need c (rms speed of Ar atom). Use:

$$c = \left(\frac{3RT}{M}\right)^{1/2} \qquad M(Ar) = 39.95\ g/mol$$

$$c = \left(\frac{3\cdot 8.31147\ J\,K^{-1}\,mol^{-1}\cdot 298\,K}{39.95\ g\,mol^{-1}}\right)^{1/2}$$

convert $g \to kg$, $J \to kg\,m^2\,s^{-2}$

$$= \left(\frac{3\cdot 8.31147\ \cancel{kg}\,m^2\,s^{-2}\,\cancel{K^{-1}}\,\cancel{mol^{-1}}\cdot 298\,\cancel{K}}{0.03995\ \cancel{kg}\,\cancel{mol^{-1}}}\right)^{1/2}$$

$$= \left(185993.8\ m^2 s^{-2}\right)^{1/2} = 431.27\ m\,s^{-1}$$

units make sense

(a) $p = 10\ bar = 10^6\ Pa = 10^6\ N\,m^{-2} = 10^6\ kg\,m^{-1}\,s^{-2}$

$$z = \frac{2^{1/2}\cdot 6.02214\times10^{23}\ \cancel{mol^{-1}}\cdot 0.36\,(10^{-9}\,\cancel{m})^2\cdot 431.27\,\cancel{m}\,s^{-1}\cdot 10^6\,\cancel{kg}\,\cancel{m^{-1}}\,\cancel{s^{-2}}}{8.31447\,\underbrace{(\cancel{kg}\,\cancel{m^2}\,\cancel{s^{-2}})}_{J}\,\cancel{K^{-1}}\,\cancel{mol^{-1}}\cdot 298\,\cancel{K}}$$

$$= 5.34\times10^{10}\ s^{-1}$$ (i.e. 5.34×10^{10} collisions per second)

(b) Plug in again or note $100\ kPa = 10^5\ Pa$, so the answer must be the answer to (a) divided by 10 $\Rightarrow z = 5.34\times10^9\ s^{-1}$

(c) $p = 1\ Pa \Rightarrow z = 5.34\times10^4\ s^{-1}$

5. (Atkins 1.35)

(a) (i) 1.0 mol, 273.15 K, 22.414 dm^3 perfect gas:

$$p = \frac{nRT}{V} = \frac{(1\ mol)(0.083145\ dm^3\text{-}bar\ K^{-1}mol^{-1})(273.15\ K)}{22.414\ dm^3}$$

$$= 1.013\ bar$$

(ii) 1.0 mol, 1000 K, 100 cm^3 = 0.1 dm^3, perfect gas:

$$p = \frac{(1\ mol)(0.083145\ dm^3\text{-}bar\ K^{-1}mol^{-1})(1000\ K)}{0.1\ dm^3} = 831.4\ bar$$

(b) (i) same as (a)(i) but van der Waals EOS:

C_2H_6: $a = 5.507\ atm\ dm^6\ mol^{-2}$ $\quad b = 6.51\times10^{-2}\ dm^3\ mol^{-1}$

$$p = \frac{nRT}{V-nb} - \frac{an^2}{V^2} = \frac{(1.0\ mol)(0.083145\ dm^3\text{-}bar K^{-1}mol^{-1})(273.15\ K)}{22.414\ dm^3 - (1.0\ mol)(6.51\times10^{-2}\ dm^3\ mol^{-1})}$$

$$- \frac{(5.507\ atm\ dm^6\ mol^{-2})(1.0\ mol)^2}{(22.414\ dm^3)^2}$$

$$= 1.016\ bar - \underbrace{0.011\ atm}_{=0.011\ bar} = 1.005\ bar$$

Note: $550\ atm \left(\frac{1.013\ bar}{atm}\right) = 557\ bar$

(ii) $$p = \frac{(1.0\ mol)(0.083145\ dm^3\text{-}bar\ K^{-1}mol^{-1})(1000\ K)}{0.1\ dm^3 - (1.0\ mol)(6.51\times10^{-2}\ dm^3\ mol^{-1})}$$

$$- \frac{(5.507\ atm\ dm^6\ mol^{-2})(1.0\ mol^2)}{(0.1\ dm^3)^2} = 2383\ bar - 550.7\ atm$$

$$= 1825\ bar$$

Note: Under conditions (i) the perfect gas and van der Waals eqs. give very similar results (pressure is relatively low), but under conditions (ii) the two equations give quite different results (pressure is higher).

6. (Atkins 1.32)

Virial: $p = \frac{RT}{V_m}\left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \ldots\right)$

Our strategy is to put VDW eq into similar form and compare.

VDW: $p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} = \frac{RT}{V_m}\left(\frac{1}{1 - b/V_m} - \frac{a/RT}{V_m}\right)$

Use expansion $\frac{1}{1-x} = 1 + x + x^2 + \ldots$ where $x = \frac{b}{V_m}$

$$\frac{1}{1 - b/V_m} = 1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \ldots$$

$$p = \frac{RT}{V_m}\left(1 + \frac{b - a/RT}{V_m} + \frac{b^2}{V_m^2} + \ldots\right)$$

Comparing the Virial and VDW eqs, we equate the coefficient of a given power of $\frac{1}{V_m}$

$$B = b - \frac{a}{RT} \qquad C = b^2$$

7.

Reaction (balanced eq) is:

$N_2 + 3H_2 \rightarrow 2NH_3$ 3 moles H_2 and 1 mole N_2 consumed to form 2 moles NH_3

	H_2	N_2	NH_3	total	
initial:	3	2	—	5	(moles)
final:	—	1	2	3	

Assume perfect gas: $pV = nRT$

n = total moles of gas

$$p = \frac{nRT}{V} = \frac{3\,\text{mol}\,(8.31447\cdot 10^{-2}\,\text{L bar K}^{-1}\text{mol}^{-1})(273.15\,\text{K})}{44.8\,\text{L}}$$

$$\boxed{p = 1.5\ \text{bar} \quad \text{total pressure}}$$

partial pressures:

$p_{H_2} = 0$

mole fraction

$p_{N_2} = x_{N_2}\,p = \frac{1}{3}\cdot 1.5\ \text{bar} = 0.5\ \text{bar}$

$p_{NH_3} = x_{NH_3}\,p = \frac{2}{3}\cdot 1.5\ \text{bar} = 1.0\ \text{bar}$