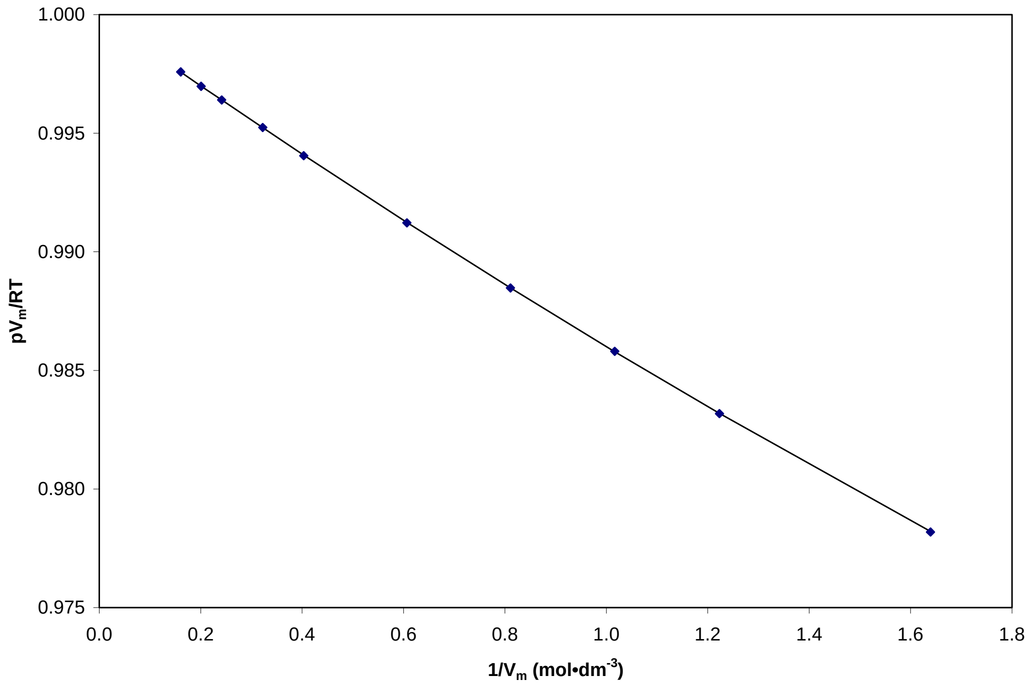
Quiz 1
CHEM 323
Fall 2008

Name: ____

1. (5 Points) When written in terms of the molar volume, V_m, the virial equation of state may be written as $pV_m = RT\left(1 + \frac{B}{V_m} + \frac{C}{V_m^2}\right)$, where p is the pressure, R the gas constant, and B and C are constants for a particular gas at a temperature, T. Data from the 300-K isotherm for argon were graphed as shown below and then fit to a quadratic of the form $y = \alpha x^2 + \beta x + \gamma$. The parameters α, β and γ were determined to be $\alpha = 0.001078 \pm 0.00004$ mol^{-2}·dm^6, $\beta = -0.01504 \pm 0.00007$ mol^{-1}·dm^3, and $\gamma = 0.99997 \pm 0.00002$ (all uncertainties at 95% confidence). What are B and C for argon at this temperature?



Rearranging the virial equation to $\frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2}$ yields a quadratic equation in $1/V_m$. By inspection it is clear that $B = \beta$ and $C = \alpha$. Therefore, $B = -0.01504 \pm 0.00007$ mol^{-1}·dm^3 and $C = 0.001078 \pm 0.00004$ mol^{-2}·dm^6.

2a. (8 Points) The Boyle temperature may be defined in terms of the compression factor, Z, and the molar volume, V_m, according to the expression $\lim_{V_m \to \infty} \frac{dZ}{d(1/V_m)} = 0$. Starting from the equation for the compression factor of a van der Waals gas, $Z = \frac{V_m}{V_m - b} - \frac{a}{V_m RT}$, show that $\frac{dZ}{d(1/V_m)} = \frac{V_m^2 b}{(V_m - b)^2} - \frac{a}{RT}$.

Potentially useful equations: $\left(\frac{\partial x}{\partial y}\right)_g \left(\frac{\partial y}{\partial z}\right)_g = \left(\frac{\partial x}{\partial z}\right)_g$, $\frac{dx^n}{dx} = nx^{n-1}$, $d(fg) = fdg + gdf$, and $d\frac{f}{g} = \frac{gdf - fdg}{g^2}$ (where f and g are functions in the same variable, and x, y and z are variables).

Using the chain rule we may rewrite the derivative as $\frac{dZ}{d(1/V_m)} = \left(\frac{dZ}{dV_m}\right)\left(\frac{dV_m}{d(1/V_m)}\right)$**.**

And since $\left(\frac{dV_m}{d(1/V_m)}\right) = \frac{d(1/V_m)^{-1}}{d(1/V_m)} = -\left(\frac{1}{V_m}\right)^{-2} = -V_m^2$**, the derivative in question may be written as** $\frac{dZ}{d(1/V_m)} = -V_m^2\left(\frac{dZ}{dV_m}\right)$**. Taking the derivative of Z with respect to V_m yields** $\left(\frac{dZ}{dV_m}\right) = \left(\frac{(V_m - b)(1) - (V_m)(1)}{(V_m - b)^2}\right) + \frac{a}{V_m^2 RT} = \left(\frac{-b}{(V_m - b)^2}\right) + \frac{a}{V_m^2 RT}$**. Substituting this result into the expression for** $\frac{dZ}{d(1/V_m)}$ **gives**

$\frac{dZ}{d(1/V_m)} = -V_m^2\left(\frac{-b}{(V_m - b)^2}\right) + \frac{a}{V_m^2 RT} = \left(\frac{V_m^2 b}{(V_m - b)^2}\right) - \frac{a}{RT}$**, which is what we sought to prove.**

b. (5 Points) Given that $\frac{dZ}{d(1/V_m)} = \frac{V_m^2 b}{(V_m - b)^2} - \frac{a}{RT}$ for a van der Waals gas, derive an expression for the Boyle temperature of a van der Waals gas in terms of the van der Waals coefficients.

To determine the Boyle temperature we evaluate $\lim_{V_m \to \infty} \frac{dZ}{d(1/V_m)} = 0$**. Substituting in the derivative for a van der Waals gas gives** $\lim_{V_m \to \infty} \frac{V_m^2 b}{(V_m - b)^2} - \frac{a}{RT}$**. In the limit of large V_m (i. e., $V_m >> b$), this becomes** $\frac{V_m^2 b}{(V_m)^2} - \frac{a}{RT} = b - \frac{a}{RT}$**. At the Boyle temperature this equals 0 (i. e.,** $b - \frac{a}{RT} = 0$**), and when solved for T gives** $T = \frac{a}{Rb}$**.**

c. (3 Points) What is the Boyle temperature for an ideal gas? Explain using $\lim_{V_m \to \infty} \frac{dZ}{d\left(1/V_m\right)} = 0$.

An ideal gas is one in which *Z* = 1 for all *T*. Therefore, the derivative $\frac{dZ}{d\left(1/V_m\right)} = 0$ for all temperatures and the Boyle temperature is not uniquely defined (there are an infinite number of temperatures for which the equation holds). So, there is no Boyle temperature for an ideal gas. *Note that I would have also accepted 0 K by the same logic.*