Quiz 4
CHEM 323
Fall 2008

Name: ____

1a. (6 Points) The variation of a certain liquid's volume as a function of temperature may be fit to the function $V = V_{300}\left(0.75 + 3.7x10^{-4}T + 1.48x10^{-6}T^2\right)$, where V_{300} is the volume at 300.0 K and the temperature is in Kelvin. Derive an expression that describes the dependence of the expansion coefficient, α, on temperature.

From the definition of the expansion coefficient, $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ **, we will first need to find** $\left(\frac{\partial V}{\partial T}\right)_p$ **, which we can do from the given expression for** $V(T)$**.**

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{\partial}{\partial T}V_{300}\left(0.75 + 3.7x10^{-4}T + 1.48x10^{-6}T^2\right)$$

$$\left(\frac{\partial V}{\partial T}\right)_p = V_{300}\frac{\partial}{\partial T}\left(0.75 + 3.7x10^{-4}T + 1.48x10^{-6}T^2\right)$$

$$\left(\frac{\partial V}{\partial T}\right)_p = V_{300}\left(3.7x10^{-4} + 2.96x10^{-6}T\right)$$

And thus, α is

$$\alpha = \frac{V_{300}\left(3.7x10^{-4} + 2.96x10^{-6}T\right)}{V_{300}\left(0.75 + 3.7x10^{-4}T + 1.48x10^{-6}T^2\right)} = \frac{3.7x10^{-4} + 2.96x10^{-6}T}{0.75 + 3.7x10^{-4}T + 1.48x10^{-6}T^2}$$

b. (4 Points) Determine α at 310.0 K.

$$\alpha = \frac{\left(3.7x10^{-4}\ \mathrm{K}^{-1}\right) + \left(2.96x10^{-6}\ \mathrm{K}^{-2}\right)T}{0.75 + \left(3.7x10^{-4}\ \mathrm{K}^{-1}\right)T + \left(1.48x10^{-6}\ \mathrm{K}^{-2}\right)T^2}$$

$$\alpha = \frac{\left(3.7x10^{-4}\ \mathrm{K}^{-1}\right) + \left(2.96x10^{-6}\ \mathrm{K}^{-2}\right)\left(310.0\ \mathrm{K}\right)}{0.75 + \left(3.7x10^{-4}\ \mathrm{K}^{-1}\right)\left(310.0\ \mathrm{K}\right) + \left(1.48x10^{-6}\ \mathrm{K}^{-2}\right)\left(310.0\ \mathrm{K}\right)^2}$$

$$\alpha = \frac{\left(0.00037 + 0.000917_6\right)\mathrm{K}^{-1}}{0.75 + 0.11_4 + 0.142_2} = \frac{0.00128_7\ \mathrm{K}^{-1}}{1.00_6} = 0.00128\,\mathrm{K}^{-1}$$

2a. (9 Points) Using the equation $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$, derive its counterpart in terms of enthalpy: $\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V$. Helpful hint: start with the definition of *H* and remember the properties of partial derivatives.

Start with the definition of enthalpy, $H = U + pV$, and convert to a differential to give $dH = dU + pdV + Vdp$. Form the derivative with respect to *V* and impose constant *T*.

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + p\left(\frac{\partial V}{\partial V}\right)_T + V\left(\frac{\partial p}{\partial V}\right)_T$$

Substitute in the given expression and simplify.

$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p + p + V\left(\frac{\partial p}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V + V\left(\frac{\partial p}{\partial V}\right)_T$$

Multiply both sides by $\left(\frac{\partial V}{\partial p}\right)_T$.

$$\left(\frac{\partial H}{\partial V}\right)_T\left(\frac{\partial V}{\partial p}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial p}\right)_T + V\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial p}\right)_T$$

Since it is a property of derivatives that $\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial x}\right)_z = 1$, we may write $\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial p}\right)_T + V$. Using the Euler chain relation, we can then write $\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial p}\right)_T\left(\frac{\partial T}{\partial V}\right)_p = -1$, from which follows $\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$.

Substituting this result into the last equation for $\left(\frac{\partial H}{\partial p}\right)_T$ gives $\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V$.

b. (5 Points) Show that $\left(\frac{\partial H}{\partial p}\right)_T = 0$ for an ideal gas.

For an ideal gas $pV = nRT$ **, which may be rearranged to** $V = \frac{nRT}{p}$**. Differentiating with respect to** T **at constant** p **gives** $\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial}{\partial T}\left(\frac{nRT}{p}\right)\right)_p = \frac{nR}{p}$**. Substituting this result into the expression for** $\left(\frac{\partial H}{\partial p}\right)_T$ **yields**

$$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V = -\frac{nRT}{p} + V = -V + V = 0.$$