

Quiz 2
CHEM 323
Fall 2008

Name: _____

1. (5 Points) A gas is described by the equation of state $p(V - nb) = nRT$, where b is a constant and the other variables have their usual meaning. If the pressure and temperature are such that V_m for the gas equals $10.0b$, what is the numerical value of the compression factor, Z ?

Potentially useful equations: $Z = \frac{V_m}{V_0}$, $pV = nRT$

Solve the given equation of state for V with $n = 1$ (re-label as V_m) to give $V_m = \frac{RT}{p} + b$.

Under the specified conditions $V_m = 10b$, substituting this into the last equation allows us to solve for b in terms of R , T and p , giving $b = \frac{RT}{9.0p}$.

The compression factor is defined as $Z = \frac{V_m}{V_0}$ where V_0 is the volume of an ideal gas under the same conditions as the non-ideal gas. Solving the ideal gas equation for V with $n = 1$ gives $V_0 = \frac{RT}{p}$. Substituting in the expressions for V_0 and V_m gives

$$Z = \frac{10b}{\left(\frac{RT}{p}\right)}. \text{ With the final substitution for } b \text{ gives } Z = \frac{10.0\left(\frac{RT}{9p}\right)}{\left(\frac{RT}{p}\right)} = \frac{10.0}{9.0} = 1.1.$$

Therefore, under these conditions $Z = 1.1$.

Note that I've changed the given value of V_m to clarify the number of significant figures in this problem. I didn't take off anything for significant figures on the quiz.

2. (4 Points) The van der Waals equation of state for a gas predicts a physically unrealistic oscillation of the pressure as a function of volume for certain isotherms. What are these oscillations called, what do they signify and how are they eliminated?

The oscillations are called the van der Waals loops. They arise when the two terms in the van der Waals equation are of similar magnitude, which in turn comes about when the cohesive and dispersive forces within the gas are balanced (i. e., the gas is condensing into a liquid). They are eliminated by the Maxwell construction which draws a horizontal line through the van der Waals loops on a p as a function of V graph, such that the area in the loops above and below the line are equal.

3. Calculate ΔU , q and w for each of the following reversible processes assuming that you have 1.00 mole of an ideal gas with a molar constant volume heat capacity, $C_{v,m}$, equal to $\frac{3}{2}R$.
- a) (5 Points) An isothermal expansion at 300.0 K from a volume of 22.4 L to a volume of 44.8 L.

For an ideal gas the internal energy depends only on T . Since T is constant, the internal energy can't change and $\Delta U = 0$. Because $\Delta U = q + w = 0$, $q = -w$.

The work involved in a reversible isothermal expansion is given by $w = -nRT \ln\left(\frac{V_f}{V_i}\right)$.

Substituting in the appropriate values gives

$$w = -(1.00 \text{ mole})(8.31447 \text{ J}\cdot\text{K}^{-1}\cdot\text{mole}^{-1})(300.0 \text{ K})\ln\left(\frac{44.8 \text{ L}}{22.4 \text{ L}}\right) = -1.73 \text{ kJ}$$

Therefore, for this process $\Delta U = 0$, $w = -1.73 \text{ kJ}$ and $q = +1.73 \text{ kJ}$.

Since $\Delta T = 0$, you can't use $C_{v,m} = \left(\frac{\partial U}{\partial T}\right)_v$ to justify $\Delta U = 0$ as this equation is not applicable when T is constant (only when V is constant).

Note that isothermal means $\Delta T = 0$, not $q = 0$! The process is performed such that the temperature of the system does not change (for example in a large water bath which can absorb heat from the system and pass it off to the rest of the universe while maintaining a constant temperature). If the change were adiabatic, then $q = 0$ but $\Delta T \neq 0$ because the system has no way to rid itself of any heat generated during the process (the system's walls do not allow passage of heat).

*A note on grading: you needed to give some basic explanation why $\Delta U = 0$ and how you know $q = -w$ (i. e., the first paragraph above). You also needed to show the proper number of significant figures throughout the problem (significant figure errors are denoted **SF**). Since ΔU , w and q can be either positive or negative, you need to show the sign (even if positive).*

- b) (5 Points) An isochoric heating at a volume of 44.8 L from 300.0 K to 400.0 K.

As there is no change in volume, $w = 0$. Since $\Delta U = q + w$ and $w = 0$, $\Delta U = q$.

At constant volume we use the constant volume heat capacity to describe changes in the internal energy when T is changed. Integrating the given expression

$$C_{v,m} = \left(\frac{\partial U}{\partial T}\right)_v, \text{ assuming } C_{v,m} \text{ is constant, gives } \Delta U = nC_{v,m}\Delta T. \text{ Substituting in the}$$

given values results (remember that $C_{v,m} = \frac{3}{2}R$) into this expression gives

$$\Delta U = (1.00 \text{ mole}) \left(\frac{3}{2} (8.31447 \text{ J}\cdot\text{K}^{-1}\cdot\text{mole}^{-1}) \right) (+100.0 \text{ K}) = +1.25 \text{ kJ}$$

Therefore, for this process $\Delta U = +1.25 \text{ kJ}$, $q = +1.25 \text{ kJ}$ and $w = 0$.

Note that you can't use $w = -p\Delta V = -nR\Delta T$ (from the ideal gas law) to find work. This expression would only be valid if there were a change in V as the result of a change in temperature. As we have no volume change (the process is isochoric), there can be no work. To receive full credit for this problem you would have needed to state this.

Potentially useful things: $\Delta U = q + w$, $w = -p\Delta V$, $w = -nRT \ln\left(\frac{V_f}{V_i}\right)$, $C_{v,m} = \left(\frac{\partial U}{\partial T}\right)_v$

$R = 8.31447 \text{ J}\cdot\text{K}^{-1}\cdot\text{mole}^{-1}$, $R = 0.0820574 \text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mole}^{-1}$, $1 \text{ L}\cdot\text{atm} = 101.325 \text{ J}$