Homework Problems
(#1-#8)
Section Questions Q1.5,Q1.14,Q2.2,Q2.8 (E&R)[4th] ed

1. For an ideal gas $P\overline{V} = RT$ $\left(\overline{V} \equiv V_m \equiv \frac{V}{n}\right.$ molar volume$)$ evaluate:

a. $\left(\frac{\partial P}{\partial \overline{V}}\right)_T$

b. $\left(\frac{\partial \overline{V}}{\partial T}\right)_P$

c. $\left(\frac{\partial T}{\partial P}\right)_{\overline{V}}$

d. $\left(\frac{\partial P}{\partial \overline{V}}\right)_T \left(\frac{\partial \overline{V}}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_{\overline{V}}$

e. One can often get, via the chain rule for differentiation, rigorous results by "canceling ∂'s" . However the correct result for part d is **NOT** what one would obtain by just "canceling ∂'s" in the numerators and denominators in each of the three terms. Why for part d can one NOT apply the chain rule to get $\left(\frac{\partial P}{\partial P}\right) = 1$? [NOTE: you may evaluate part d and e using the specific results from a, b, c for an ideal gas. However the correct result is a more general relationship for any well behaved function z(x,y)]

2. For a Van der Waals gas: $\left(P + \frac{a}{\overline{V}^2}\right)\left(\overline{V} - b\right) = RT$ evaluate:

a. $\left(\frac{\partial P}{\partial \overline{V}}\right)_T$

b. $\left(\frac{\partial^2 P}{\partial \overline{V}^2}\right)_T$

c. $\left(\frac{\partial P}{\partial T}\right)_{\overline{V}}$

d. $\left[\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial \overline{V}}\right)_T\right]_{\overline{V}}$

e. $\left[\frac{\partial}{\partial \overline{V}}\left(\frac{\partial P}{\partial T}\right)_{\overline{V}}\right]_T$

f. How do the results of parts d and e compare? Why is this?

3. E&R P1.38 (4th edition)

★**4.** ***(optional)*** The Van der Waals and virial expressions are two commonly used equations of state as approximations to real gas behavior:

$$P = \frac{RT}{(\overline{V} - b)} - \frac{a}{\overline{V}^2} \quad \textit{Van der Waals}$$

$$P = RT\left[\frac{C_1(T)}{\overline{V}} + \frac{C_2(T)}{\overline{V}^2} + \frac{C_3(T)}{\overline{V}^3} \dots + \frac{C_n(T)}{\overline{V}^n} \dots\right] \quad \textit{virial}$$

a. Show that the first three virial coefficients are related to the Van der Waals parameters a and b in the following way:

$C_1(T)=1$

$C_2(T)=b-a/RT$

$C_3(T)=b^2$

HINT:

note that the virial expansion is just a Taylor (Maclaurin) series in $z^k = \left(\frac{1}{\overline{V}}\right)^k$

$$\frac{P}{RT} = \sum_{k=0}^{\infty} C_k(T)\left(\frac{1}{\overline{V}}\right)^k = \sum_{k=0}^{\infty} C_k(T) z^k = f(z;T)$$

$$\textit{with coefficient } C_k(T) = \frac{1}{k!}\left(\frac{d^k f}{dz^k}\right)_{z=0}$$

b. Why does the Van der Waals "a" only appear in $C_2(T)$?

5. Limiting cases:

a. ***(required)***

The residual volume of a gas is defined as:

$$\overline{V}_{res} = \lim_{P \to 0}\left(\overline{V} - \frac{RT}{P}\right)$$

If a gas has the equation of state

$$P\overline{V}(1-\alpha P) = RT$$

what is $\overline{V}_{res}$?

★b. ***(optional)*** Engel & Reid P1.33

6. E&R P2.10 *[4th ed]*

AND IN ADDITION
calculate q for each of the irreversible and reversible processes in parts a and b.
all answers should be in energy units of joules (J).

7. One mole of ideal gas is heated reversibly at a constant pressure of 1 atm from 273.15 K to 373.15 K

a. Compute the work involved in the process.

b. If the gas were expanded reversibly and isothermally at 273.15 K from an initial pressure of 1 atm, what would the final pressure need to be in order to equal the work calculated in part a?

★**8.** (optional) A gas has the equation of state $P\overline{V} = RT + \alpha(T)P$

a. Show that for a reversible expansion between T_1 and T_2 at constant pressure P, the work done is:

$$w = nR(T_1 - T_2) + n\left(\alpha(T_1) - \alpha(T_2)\right)P$$

b. Show that for a reversible expansion between V_1 and V_2 at constant temperature T, the work done is:

$$w = nRT\ln\left[\frac{\overline{V}_1 - \alpha(T)}{\overline{V}_2 - \alpha(T)}\right]$$