Homework Problems
(#1-#4)

1. For an ideal gas $P\overline{V} = RT \quad (\overline{V} \equiv V_m \equiv \frac{V}{n} \quad \textit{molar volume})$ 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. Engel & Reid problem P1.3

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

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

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

a. Show that the first three virial coefficients are related top 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 $z^k = \left(\frac{1}{\bar{V}}\right)^k$

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

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

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