Homework Problems
(#1-#8)

1. For an ideal gas $P\bar{V} = RT$ $(\bar{V} \equiv V_m \equiv \dfrac{V}{n}$ *molar volume*) evaluate:

a. $\left(\dfrac{\partial P}{\partial \bar{V}}\right)_T$

b. $\left(\dfrac{\partial \bar{V}}{\partial T}\right)_P$

c. $\left(\dfrac{\partial T}{\partial P}\right)_{\bar{V}}$

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

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 $\left(\dfrac{\partial P}{\partial P}\right) = 1$? [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: $\left(P + \dfrac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT$ evaluate:

a. $\left(\dfrac{\partial P}{\partial \bar{V}}\right)_T$

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

c. $\left(\dfrac{\partial P}{\partial T}\right)_{\bar{V}}$

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

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

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

3. Engel & Reid problem P1.3 *[numbers differ from E&R 2nd edition]*
   Calculate the pressure exerted by Ar for a molar volume of 1.31 L mol^{-1} at 426K using the van der Waals equation of state. The van der Waals parameters *a* and *b* for Ar are 1.355 bar dm^6 mol^{-2} and 0.0320 dm^3 mol^{-1}, respectively. Is the attractive or repulsive portion of the potential dominant under these conditions?

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

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

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

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 $z^k = \left(\frac{1}{\overline{V}}\right)^k$

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

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

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:

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

        If a gas has the equation of state

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

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

  ★b. **(optional)** Engel & Reid P1.37 *[same as E&R 2ⁿᵈ edition]*

6. E&R P2.6 *[numbers differ from E&R 2ⁿᵈ edition]*
A 1.50 mole sample of an ideal gas at 28.5°C expands isothermally from an
initial volume of 22.5 dm^3 to a final volume of 75.5 dm^3. Calculate w for this
process (a) for expansion against an external pressure of 0.498 $\times 10^5$ Pa, and (b)
for a reversible expansion.
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 $P\bar{V} = RT + \alpha(T)P$

    a. Show that for a reversible expansion between T_1 and T_2 at constant pressure P, the
       work done is:
$$w = nR(T_1 - T_2) + n(\alpha(T_1) - \alpha(T_2))P$$

    b. Show that for a reversible expansion between V_1 and V_2 at constant temperature T,
       the work done is:
$$w = nRT \ln\left[\frac{\bar{V}_1 - \alpha(T)}{\bar{V}_2 - \alpha(T)} \right]$$