


note: in this printout
the PowerPoint animations hide
some of the text
and links among slides are not preserved

must come to lecture (Wed, 8 Jan) for the
full HW#1 HINTS show !!!

Homework Problems (#1-#4)

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

- a. $\left(\frac{\partial P}{\partial \bar{V}}\right)_T$ 
- b. $\left(\frac{\partial \bar{V}}{\partial T}\right)_P$
- c. $\left(\frac{\partial T}{\partial P}\right)_{\bar{V}}$
- d. $\left(\frac{\partial P}{\partial \bar{V}}\right)_T \left(\frac{\partial \bar{V}}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_{\bar{V}}$

comments on math techniques 1,2
discussion section

- 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: $\left(P + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT$ evaluate:

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

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

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

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



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

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

second and mixed partial derivatives,
use parts a and c in b,d,e

3. Engel & Reid problem P1.3

hint : see E&R example problem 1.4, p12
bar ↔ atm ↔ Pa atm=1.013 bar= 1.013×10⁵ Pa
L ↔ dm³ ↔ m³ L=dm³=(10⁻¹m)³=10⁻³ m³

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

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

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

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

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

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

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

Tutorial starts TOMORROW
Thursday 9th January
7:30-8:40 PM
Physical Sciences 140

HW #1 DUE IN CLASS†
Friday, 10th January
NAME and SECTION

*† students (but **only** students) **enrolled** in
Gabe's Section 1D (Fri 2:00-3:10 PM)
may turn in HW in section or
by 5PM in CHEM 163B HW box
mail room outside PhysSci 230*

$$PV = nRT \quad P\bar{V} = RT \quad P = \frac{RT}{\bar{V}} \quad \bar{V} = \frac{V}{n} \text{ molar volume (E\&R } V_m)$$

$$(1a) \left(\frac{\partial P}{\partial \bar{V}} \right)_T = ?$$

$$\left(\frac{\partial P}{\partial \bar{V}} \right)_T = \left(\frac{\partial \frac{RT}{\bar{V}}}{\partial \bar{V}} \right)_T =$$

||
?

does result make sense ?

if sign of $\left(\frac{\partial P}{\partial \bar{V}} \right)_T > 0 \Rightarrow \text{const T: increase } \bar{V}, \text{ then P}$

$< 0 \Rightarrow \text{const T: increase } \bar{V}, \text{ then P}$



Problem #2 Van der Waals equation of state: $\left(P + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT$ (a, b, R are constants)

$$(2a) \left(\frac{\partial P}{\partial \bar{V}}\right)_T = \quad (2c) \left(\frac{\partial P}{\partial T}\right)_{\bar{V}} =$$

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

$$(2a) \left(\frac{\partial P}{\partial \bar{V}}\right)_T = \blacklozenge \quad (2c) \left(\frac{\partial P}{\partial T}\right)_{\bar{V}} = \blacklozenge$$

Use these results in 2b, 2d, 2e

$$(2b) \left(\frac{\partial^2 P}{\partial \bar{V}^2}\right)_T = \left(\frac{\partial}{\partial \bar{V}} \left(\frac{\partial P}{\partial \bar{V}}\right)_T\right)_T \left(\frac{\partial}{\partial \bar{V}} (\blacklozenge)\right)_T$$

