

Chem 531: Problem Set #5

Due in class: Tues, Oct. 17th

- (1) In class we derived the Gibbs-Helmholtz equation as the temperature dependence of the quantity $\Delta G/T$ at constant P to be $d(\Delta G/T) = -\Delta H/T^2 dT$. Use the chain rule for derivatives to derive the Gibbs-Helmholtz equation in terms of $1/T$, i.e., $d(\Delta G/T) = \Delta H d(1/T)$.
- (2) Use the van der Waals (vdW) equation of state to calculate the molar volume of CO at 200 K and 1000 bar. Compare your result to the value you would get using the ideal gas equation of state. The experimental value is $0.04009 \text{ L mol}^{-1}$. The vdW parameters of CO are $a = 1.4734 \text{ dm}^6 \text{ bar mol}^{-2}$ and $b = 0.039523 \text{ dm}^3 \text{ mol}^{-1}$.
- (3) Show that $B_{2V}(T) = RTB_{2P}(T)$, i.e., relate the 2nd virial coefficient in terms of molar volume (B_{2V}) to that from the expansion of pressure (B_{2P}).
- (4) Use the following data for $\text{NH}_3(\text{g})$ at 273 K to determine $B_{2P}(T)$ at 273 K.

P/bar	0.10	0.20	0.30	0.40	0.50	0.60	0.70
$(Z-1)/10^{-4}$	1.519	3.038	4.557	6.071	7.583	9.002	10.551

Please attach any graph needed for this problem. Using Excel is fine.

Note: to be clear, the first entry under the $P = 0.10$ bar column is $Z = 1 + 1.519 \times 10^{-4}$

- (5) The density of oxygen (O_2) as a function of pressure at 273.15 K is listed below.

P/atm	0.2500	0.5000	0.7500	1.0000
$\rho/\text{g dm}^{-3}$	0.356985	0.714154	1.071485	1.428962

Please attach any graph needed for this problem. Using Excel is fine.

Use this data to determine $B_{2V}(T)$ for oxygen. Take the atomic mass of oxygen to be 15.9994 amu and the value of the molar gas constant to be $8.31451 \text{ J K}^{-1} \text{ mol}^{-1} = 0.0820578 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$.