

Chem 531: Problem Set #5**SOLUTIONS**

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., $d(\Delta G/T) = \Delta H d(1/T)$.

$$\left(\frac{\partial \Delta G/T}{\partial 1/T} \right)_P = \left(\frac{\partial \Delta G/T}{\partial T} \right)_P \left(\frac{\partial T}{\partial 1/T} \right)$$

$$\text{but } \frac{d}{dT} \left(\frac{1}{T} \right) = -\frac{1}{T^2} \quad \text{so } d\left(\frac{1}{T}\right) = -\frac{dT}{T^2}$$

$$\text{hence } \left(\frac{dT}{d(1/T)} \right) = -T^2$$

$$\left(\frac{\partial \Delta G/T}{\partial 1/T} \right)_P = \left(\frac{\partial \Delta G/T}{\partial T} \right)_P (-T^2) = \frac{-\Delta H}{T^2} (-T^2) = \Delta H$$

$$\therefore d(\Delta G/T) = \Delta H d(1/T) \quad \text{at const. } P$$

- (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 $b = 0.039523 \text{ dm}^3 \text{ mol}^{-1}$.

van der Waals:

$$\bar{V}^3 - \left(b + \frac{RT}{P}\right)\bar{V}^2 + \frac{a}{P}\bar{V} - \frac{ab}{P} = 0$$

$$a = 1.4734 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-2}$$

$$b = 0.039523 \text{ dm}^3/\text{mol}$$

by successive approx

$$\boxed{\bar{V} = 0.049985 \text{ L mol}^{-1}}$$

(eqn differs from zero by 6.4×10^{-9})

Redlich-Kwong:

$$\bar{V}^3 - \frac{RT}{P}\bar{V}^2 - \left(B^2 + \frac{BR}{T} - \frac{A}{T^{1/2}P}\right)\bar{V} - \frac{AB}{T^{1/2}P} = 0$$

$$A = 17.208 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-2} \cdot \text{K}^{1/2}$$

$$B = 0.027394 \text{ dm}^3/\text{mol}$$

by successive approx

$$\boxed{\bar{V} = 0.038655 \text{ L/mol}} \quad (\text{eqn} = -3.0 \times 10^{-9})$$

$$\text{expt: } 0.04009 \text{ L/mol}$$

$$\text{ideal gas: } \bar{V} = \frac{RT}{P} = \boxed{0.01663 \text{ L/mol}}$$

(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}).

$$\textcircled{1} \quad \frac{P\bar{V}}{RT} = 1 + B_{2V}\left(\frac{1}{\bar{V}}\right) + B_{3V}\left(\frac{1}{\bar{V}}\right)^2 + \dots$$

$$\textcircled{2} \quad \frac{P\bar{V}}{RT} = 1 + B_{2P}P + B_{3P}P^2 + \dots$$

$$\begin{aligned} \text{from } \textcircled{1}: \quad P &= \frac{RT}{\bar{V}} \left(1 + B_{2V}\left(\frac{1}{\bar{V}}\right) + B_{3V}\left(\frac{1}{\bar{V}}\right)^2 + \dots \right) \\ &= \frac{RT}{\bar{V}} + RTB_{2V}\left(\frac{1}{\bar{V}}\right)^2 + RTB_{3V}\left(\frac{1}{\bar{V}}\right)^3 + \dots \end{aligned}$$

Substituting this into $\textcircled{2}$

$$\textcircled{3} \quad \frac{P\bar{V}}{RT} = 1 + B_{2P} \left[\frac{RT}{\bar{V}} + RTB_{2V}\left(\frac{1}{\bar{V}}\right)^2 + \dots \right] + B_{3P} \left[\frac{RT}{\bar{V}} + \dots \right]^2$$

equating powers of $\frac{1}{\bar{V}}$ between $\textcircled{1}$ and $\textcircled{3}$

$$\boxed{B_{2V} = RTB_{2P}}$$

(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 $Z = 1 + 1.519 \times 10^{-4}$

see the attached graph of Z vs. P

$$Z = 1 + B_{2P}P + B_{3P}P^2 + \dots$$

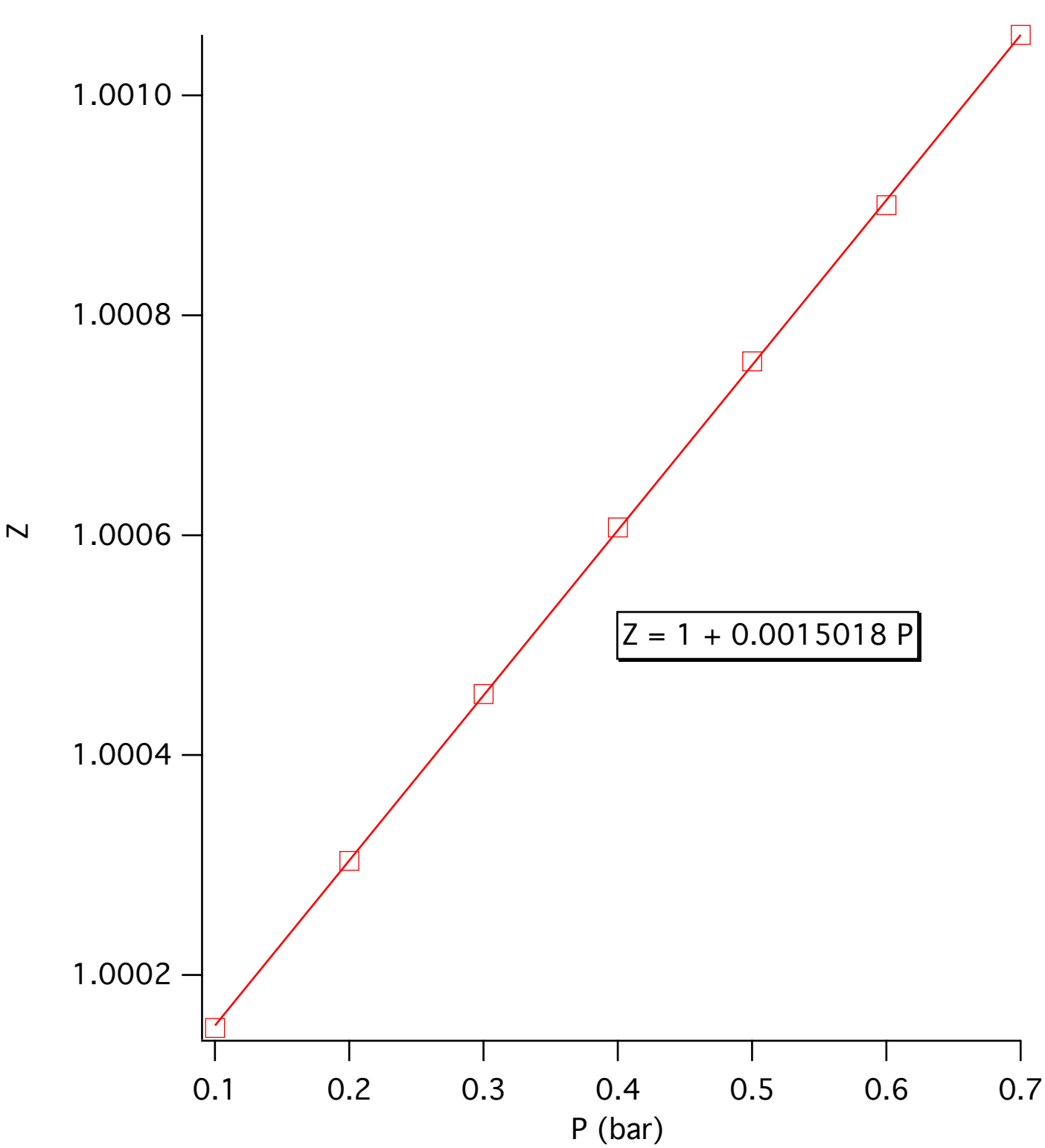
assuming only B_{2P} contributes (fit to straight line)

$$B_{2P} = 0.001502 \text{ bar}^{-1}$$

(probably only 2 sig figs though)

allowing for B_{3P} (fit to quadratic)

$$B_{2P} = 0.001536 \text{ bar}^{-1}$$



(5) The density of oxygen (O₂) 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 $8.31451 \text{ J K}^{-1} \text{ mol}^{-1} = 0.0820578 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$.

P/atm	0.2500	0.5000	0.7500	1.0000
$\rho/\text{g dm}^{-3}$	0.356985	0.714154	1.071485	1.428962
$\frac{1}{V}$	0.011562	0.0223181	0.0334852	0.0446507
z	0.999776	0.999521	0.9992802	0.999062

Convert ρ to $\frac{1}{V}$: $\frac{1}{V} = \frac{\rho}{M}$ or $\bar{V} = \frac{M}{\rho}$

Convert P and $\frac{1}{V}$ to z at 273.15 K

$$z = \frac{P\bar{V}}{RT}$$

plot $\frac{1}{V}$ vs. z $z = 1 + B_{2V}\left(\frac{1}{V}\right) + B_{3V}\left(\frac{1}{V}\right)^2 + \dots$

assuming linear, $B_{2V} = -0.02134 \text{ dm}^3$

assuming quadratic, $B_{2V} = -0.02548 \text{ dm}^3$

↳ noticeably better fit

