Quiz 7
Chemical Engineering Thermodynamics
March 3, 2016

1)
Sketch two subcritical isotherms and two supercritical isotherms. Using the isotherms, describe how the following derivatives could be obtained numerically: $(\partial P/\partial T)_V$, $(\partial V/\partial T)_P$, $(\partial P/\partial V)_T$. Compare the relative sizes of the derivatives for liquids and gases.

-Also show the critical isotherm.
-For each of these three partial derivatives sketch a piston and explain how it could be measured. For constant pressure put a weight on the piston of fixed mass. (The pressure is the force (weight*g) divided by the piston cross sectional area, A. The volume is the height of the piston times A.)

2)
7.6 N.B. Vargaftik (1975)[23] lists the following experimental values for the specific volume of isobutane at 175°C. Compute theoretical values and their percent deviations from experiment by the following:

(a) The generalized charts
(b) The Peng-Robinson equation

Do for Only One Experimental Condition: P = 3.5 MPa (Experimental: V = 13.36 cm^3/g).
P_c=3.648 MPa, T_c=408.14°K, ω=0.177, MW = 58.123 g/mole, R = 8.314 cm^3MPa/(mole°K).

-For part (a) include in your answer the chart given with the quiz showing the points where you found the values.

-For part (b) only outline how you would solve the problem. Including how the Newton-Raphson method is implemented (give the steps) and the equations you would use. Obtain all equations that you would need.
-Include a sketch of a plot of F(Z) versus Z to show how the Newton-Raphson method works.
-As an alternative to the Newton-Raphson method, how would you use Solver in Excel to find the solution for part (b)? Give the steps involved in order to demonstrate that you have (or could) used Solver for this purpose.

Maxwell's Relations

$$dU = TdS - PdV \;\Rightarrow\; -(\partial P/\partial S)_V = (\partial T/\partial V)_S \qquad 6.29$$

$$dH = TdS + VdP \;\Rightarrow\; (\partial V/\partial S)_P = (\partial T/\partial P)_S \qquad 6.30$$

$$dA = -SdT - PdV \;\Rightarrow\; (\partial P/\partial T)_V = (\partial S/\partial V)_T \qquad 6.31$$

$$dG = -SdT + VdP \;\Rightarrow\; -(\partial V/\partial T)_P = (\partial S/\partial P)_T \qquad 6.32$$

$$\left(\frac{\partial x}{\partial y}\right)_F \left(\frac{\partial y}{\partial F}\right)_x \left(\frac{\partial F}{\partial x}\right)_y = -1 \qquad 6.15$$

Triple product rule.

$$\left(\frac{\partial x}{\partial y}\right)_F = \left(\frac{\partial x}{\partial z}\right)_F \left(\frac{\partial z}{\partial y}\right)_F \qquad 6.16$$

Chain rule interposing a variable.

$$\left(\frac{\partial F}{\partial w}\right)_z = \left(\frac{\partial F}{\partial x}\right)_y \left(\frac{\partial x}{\partial w}\right)_z + \left(\frac{\partial F}{\partial y}\right)_x \left(\frac{\partial y}{\partial w}\right)_z \qquad 6.17$$

The expansion rule.

$$Z = Z^0 + \omega Z^1 \qquad 7.3$$

Peng-Robinson Equation:

The Peng-Robinson equation of state (EOS) is given by:

$$P = \frac{RT\rho}{(1-b\rho)} - \frac{a\rho^2}{1+2b\rho-b^2\rho^2} \quad \text{or} \quad Z = \frac{1}{(1-b\rho)} - \frac{a}{bRT}\cdot\frac{b\rho}{1+2b\rho-b^2\rho^2} \qquad 7.15$$

where ρ = molar density = $n/\underline{V}$, b is a constant, and a depends on temperature and acentric factor,[7]

$$a \equiv a_c\alpha; \quad a_c \equiv 0.45723553\frac{R^2T_c^2}{P_c} \qquad b \equiv 0.07779607R\frac{T_c}{P_c} \qquad 7.16$$

$$\alpha \equiv [1+\kappa(1-\sqrt{T_r})]^2 \qquad \kappa \equiv 0.37464 + 1.54226\omega - 0.26992\omega^2 \qquad 7.17$$

$$A \equiv aP/R^2T^2 \qquad 7.21$$

$$B \equiv bP/RT \qquad 7.22$$

$$b\rho = B/Z;\ a\rho/RT = A/Z \qquad 7.23$$

$$\boxed{Z = \frac{1}{(1-B/Z)} - \frac{A}{B}\cdot\frac{B/Z}{1+2B/Z-(B/Z)^2}} \qquad 7.24$$

$$Z^3 - (1-B)Z^2 + (A-3B^2-2B)Z - (AB-B^2-B^3) = 0 \qquad 7.25$$

$$Z = 1 + (B^0 + \omega B^1)P_r/T_r \quad \text{or} \quad Z = 1 + BP/RT \qquad 7.6$$

where $B(T) = (B^0 + \omega B^1)RT_c/P_c$ 7.7

$$B^0 = 0.083 - 0.422/T_r^{1.6} \qquad 7.8$$

$$B^1 = 0.139 - 0.172/T_r^{4.2} \qquad 7.9$$

Subject to $T_r > 0.686 + 0.439P_r$ or $V_r > 2.0$ 7.10

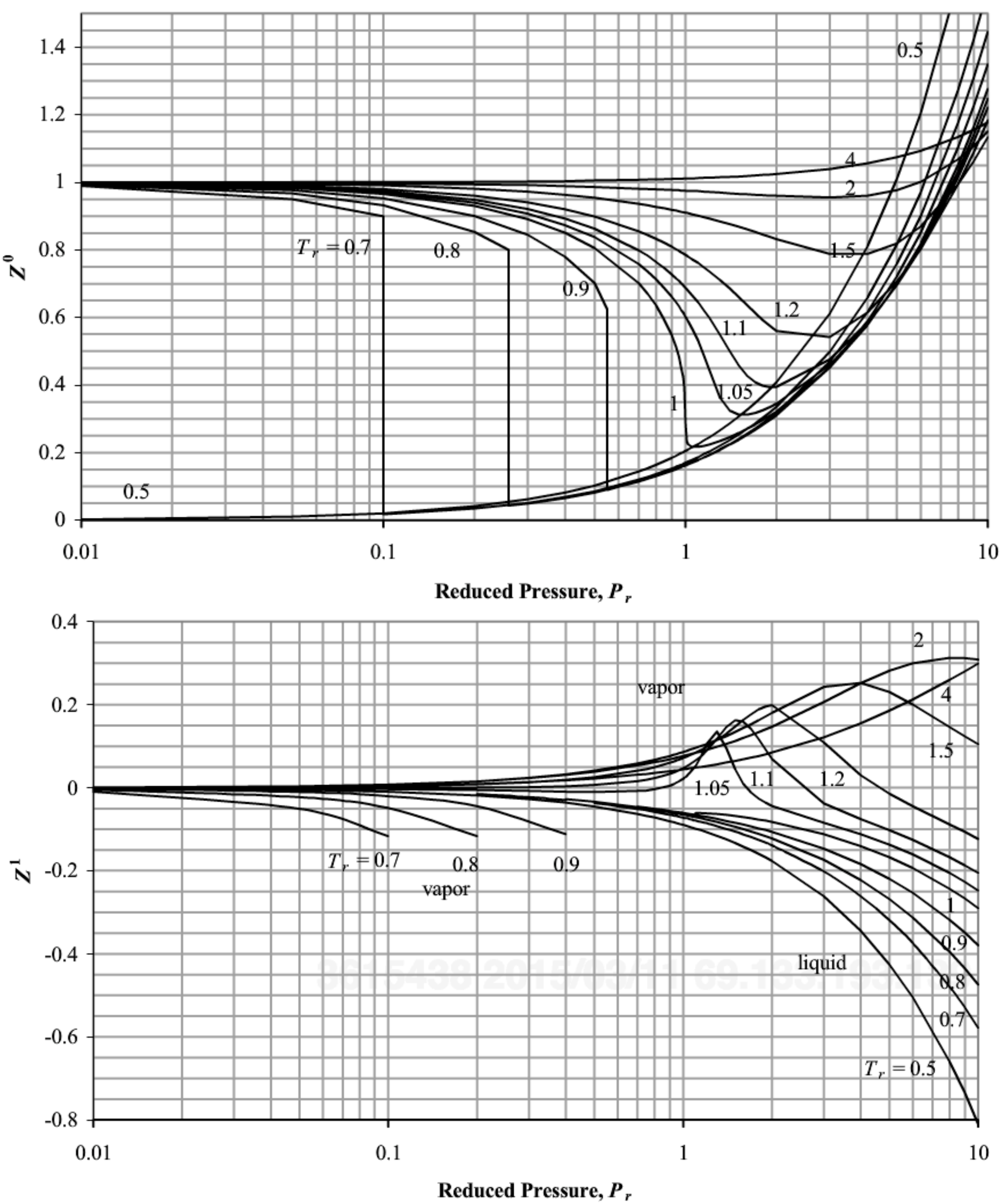

Figure 7.4 *Generalized charts for estimating the compressibility factor. (Z^0) applies the Lee-Kesler equation using $\omega = 0.0$, and (Z^1) is the correction factor for a hypothetical compound with $\omega = 1.0$. Note the semilog scale.*

Answers Quiz 7
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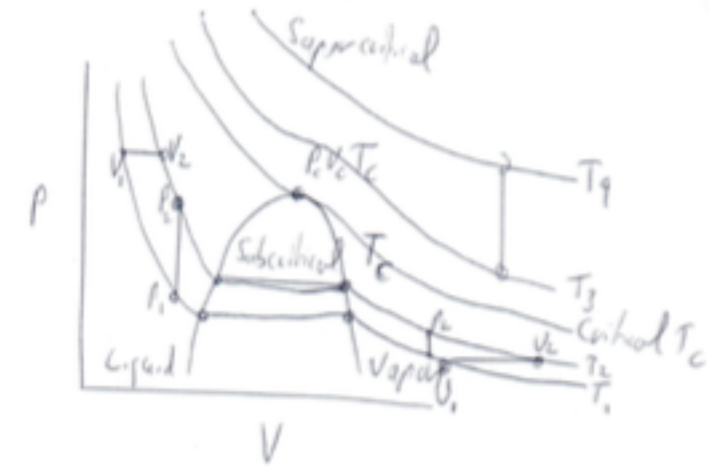
1)



$\left(\frac{\partial P}{\partial T}\right)_V$ is points on a vertical line $\left(\frac{P_2-P_1}{T_2-T_1}\right) = \left(\frac{\partial P}{\partial T}\right)_V$

Larger for Liquid since for a given ΔT, ΔP is much larger for a vapor.

$\left(\frac{\partial V}{\partial T}\right)_P$ is points on a horizontal line

$$\left(\frac{V_2-V_1}{T_2-T_1}\right) = \left(\frac{\partial V}{\partial T}\right)_P$$

Larger for a vapor since for a given ΔT, ΔV is larger for a vapor

$\left(\frac{\partial P}{\partial V}\right)_T$ is the slope of the isotherm which is lower for the Liquid since ΔV is lower [illegible]

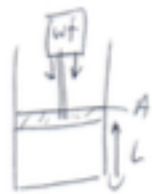
$\left(\frac{\partial P}{\partial T}\right)_V$

Measure force w/ a fixed piston position as you change temperature

$$P = \frac{F}{A}$$

$$V = LA$$

$\left(\frac{\partial V}{\partial T}\right)_P$



Measure change in L (volume) with change in T keeping the force on the piston constant

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

Change F and measure L at constant Temperature

$P = F/A \quad V = LA$

$$\left(\frac{\Delta P}{\Delta V}\right)_T \Rightarrow \left(\frac{\partial P}{\partial V}\right)_T$$

2) a)

$P = 35\ \text{Atm} = 3.5\ \text{mPa}$

$\left(V = 13.36\ \frac{cm^3}{s}\right)$

$175\,^\circ C + 273\,^\circ K = 448\,^\circ K$

isobutane

$T_c = 408\,^\circ K$

$P_c = 3.65\ \text{mPa}$

$\omega = 0.177$

$T_R = \frac{448\,^\circ K}{408\,^\circ K} = 1.10$

$P_R = \frac{3.5}{3.65} = 0.96$

$Z_0 = 0.65$

$Z_1 = 0.04$

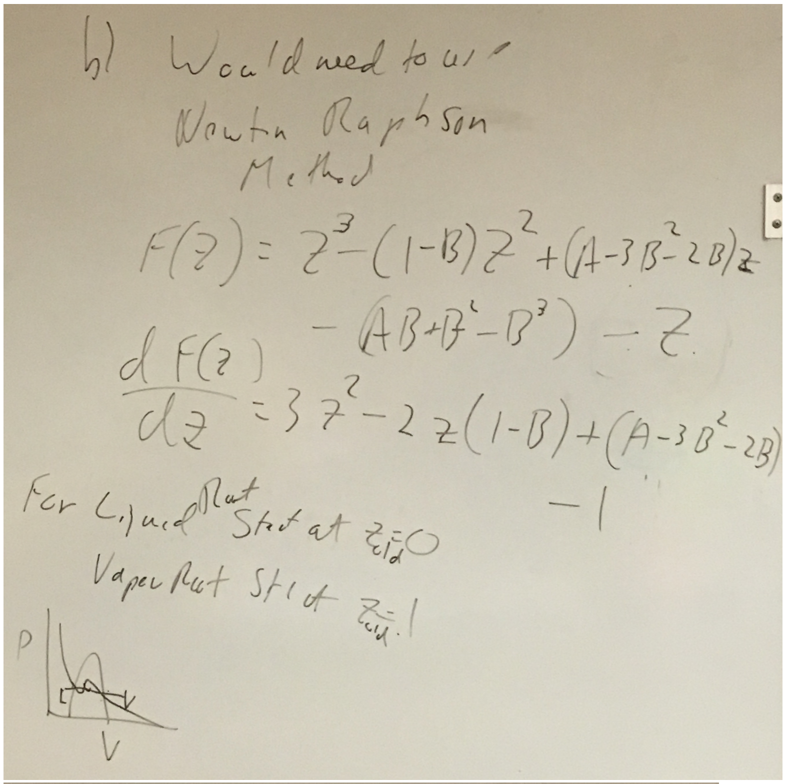
$Z = Z_0 + Z_1 \cdot \omega = 0.65 + 0.4 \cdot 0.177 = 0.66$

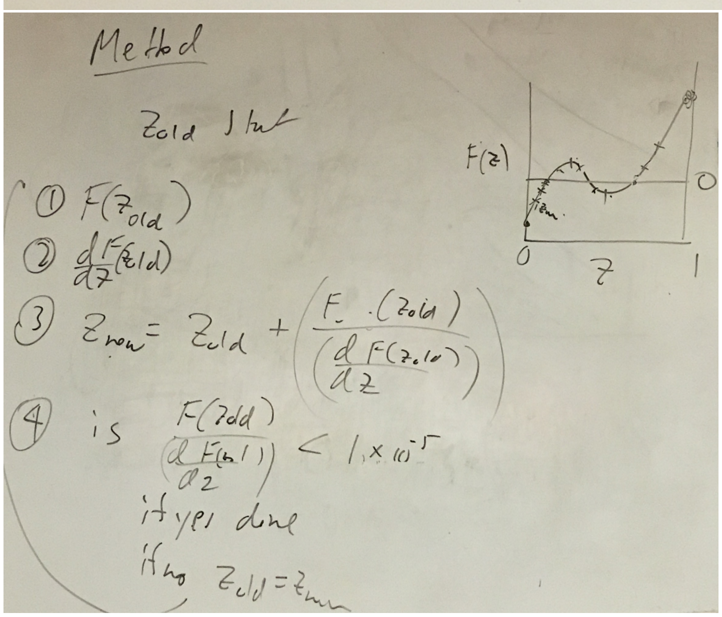
$Z = \frac{PV}{RT}$

$V = \frac{ZRT}{P} = \frac{(0.66)\ 8.314\ \frac{MPa\,cm^3}{kmol\,K}\ 448\,K}{3.5\ \text{mPa}}$

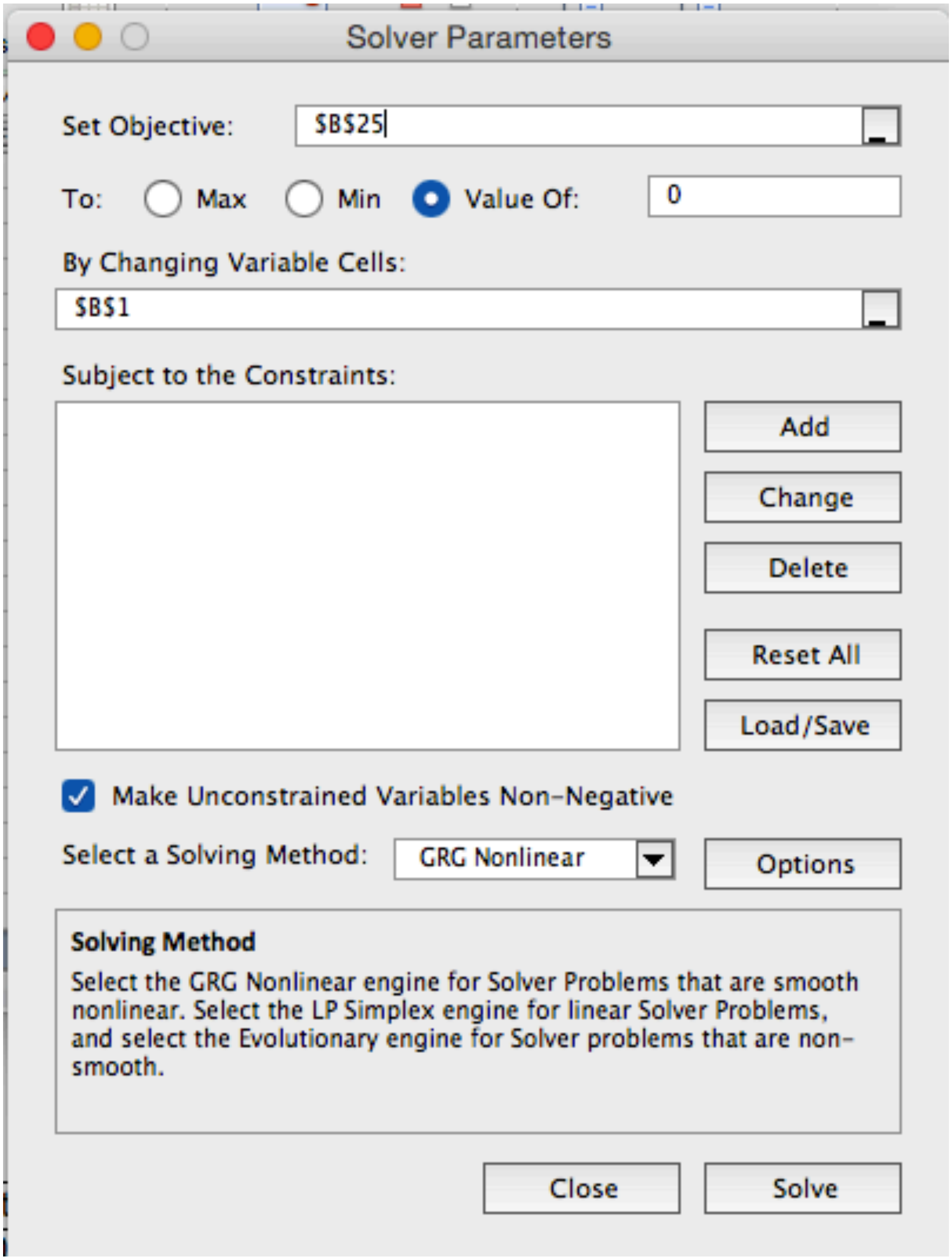
$= 702\ \text{cm}^3/\text{mole} \left(\frac{1}{58.1\ g/mol}\right)$

$V = 12.1\ \text{cm}^3/s$





Using Solver you would make two cells one for Z and one for F(Z). The F(Z) is the same F(Z) for the NR method. Then you would set the objective cell as F(Z), set the desired value to 0 by changing the Z cell and run solver to find the answer. You set the F(Z) cell by writing = the equation in the cell. You don't need dF(Z)/dZ for solver since it finds this numerically for each point.


Solver Parameters
Set Objective:
B25
To:
Max
Min
Value Of:
0
By Changing Variable Cells:
B1
Subject to the Constraints:
Add
Change
Delete
Reset All
Load/Save
Make Unconstrained Variables Non-Negative
Select a Solving Method:
GRG Nonlinear
Options
Solving Method
Select the GRG Nonlinear engine for Solver Problems that are smooth nonlinear. Select the LP Simplex engine for linear Solver Problems, and select the Evolutionary engine for Solver problems that are non-smooth.
Close
Solve