

Quiz 7
Chemical Engineering Thermodynamics
March 13, 2015

1)

6.6 Express $\left(\frac{\partial H}{\partial V}\right)_T$ in terms of α_p and/or κ_T

(Maxwell & Triple Rule given below.)

2)

7.1 The compressibility factor chart provides a quick way to assess when the ideal gas law is valid. For the following fluids, what is the minimum temperature in K where the fluid has a gas phase compressibility factor greater than 0.95 at 30 bar?

- (a) Nitrogen
- (b) Carbon dioxide
- (c) Ethanol

(Compressibility charts given below.)

	Thermodynamic Parameters		
	T_c °K	P_c MPa	ω
N ₂	126	3.41	0.040
CO ₂	304.2	7.32	0.228
EtOH	513.9	6.38	0.635

3)

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, V = 13.36 cm³/g.

P_c=3.648 MPa, T_c=408.14°K, ω=0.177, MW = 58.123 g/mole, R = 8.314 cm³MPa/(mole°K).

Compressibility charts and the Peng-Robinson equation are given below.

Maxwell's Relations

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

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

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

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

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

6.15  Triple product rule.

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

6.16  Chain rule interposing a variable.

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

6.17  The expansion rule.

Peng-Robinson Equation:

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

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

where $\rho = \text{molar density} = n/V$, b is a constant, and a depends on temperature and acentric factor,⁷

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

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

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

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

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

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

$$\text{Subject to } T_r > 0.686 + 0.439P_r \text{ or } V_r > 2.0 \quad 7.10$$

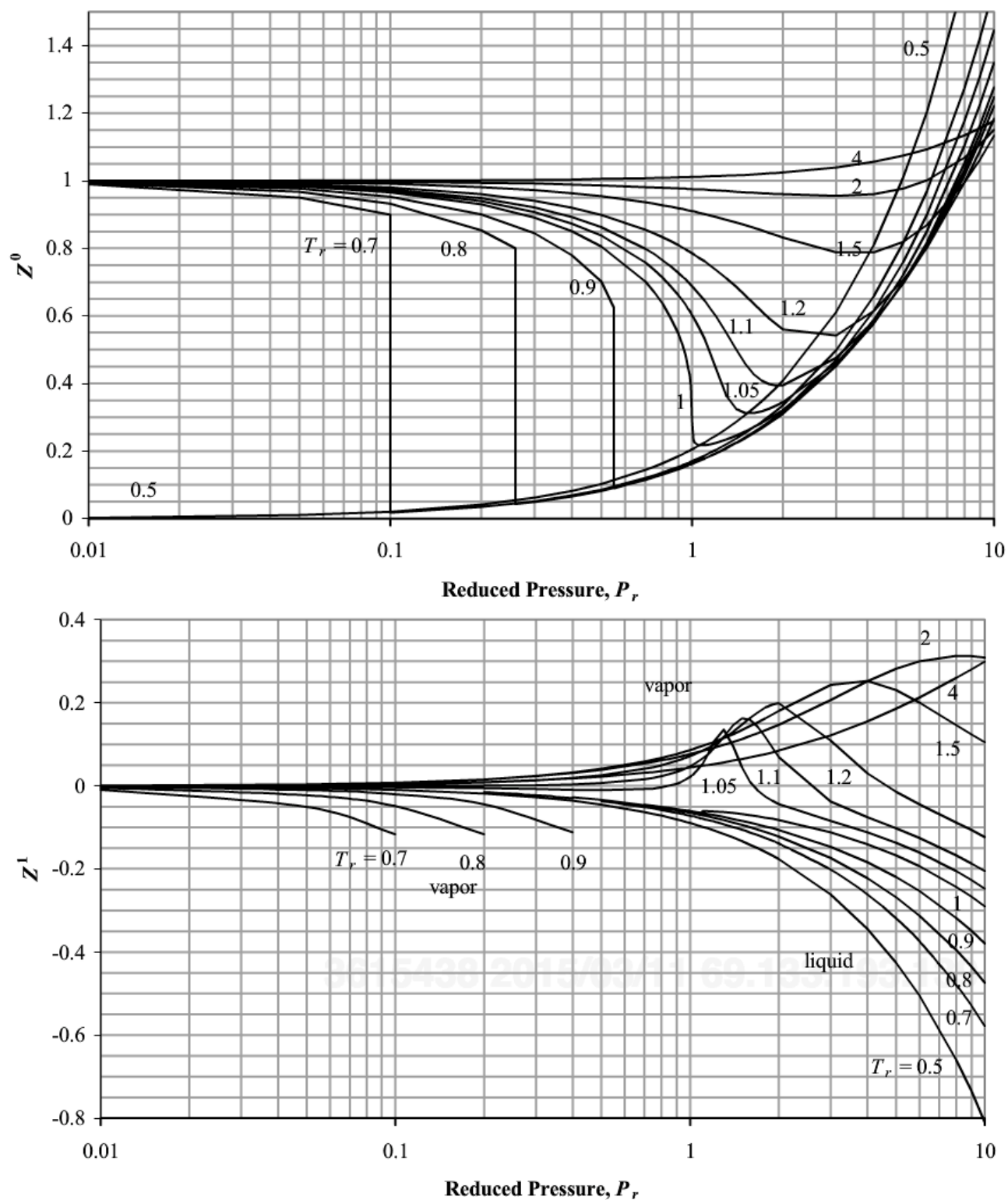


Figure 7.4 Generalized charts for estimating the compressibility factor. (Z^0) applies the Lee-Kesler equation using $\omega = 0.0$, and (Z^1) is the correction factor for a hypothetical compound with $\omega = 1.0$. Note the semilog scale.

Answers Quiz 7
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1)

6.6 Express $\left(\frac{\partial H}{\partial V}\right)_T$ in terms of α_p and/or κ_T

(Maxwell & Triple Rule given below.)

(6.06) Express $(dH/dV)_T$ in terms of ...

$$dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T + V\left(\frac{\partial P}{\partial V}\right)_T$$

$$= T\left(\frac{\partial P}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial V}\right)_T \quad \text{where} \quad \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T = \frac{\alpha_p}{\kappa_T}$$

$$= \frac{\alpha_p T - 1}{\kappa_T}$$

2)

7.1 The compressibility factor chart provides a quick way to assess when the ideal gas law is valid. For the following fluids, what is the minimum temperature in K where the fluid has a gas phase compressibility factor greater than 0.95 at 30 bar?

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(Compressibility charts given below.)

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(7.01) The compressibility factor chart provides...

- a) $Pr = 0.88$, the T limit where $Z^0 > 0.95$ is $Tr = 1.75$, $T > 220$ K
- b) $Pr = 0.41$, the T limit where $Z^0 > 0.95$ is $Tr = 1.4$, $T > 425$ K
- c) $Pr = 0.47$, the T limit where $Z^0 > 0.95$ is $Tr = 1.5$, $T > 775$ K

Therefore, it can be seen that there isn't any single temperature above which the ideal gas law is valid for all fluids; the temperature depends on the fluid.

3)

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Do for Only One Experimental Condition: $P = 3.5 \text{ MPa}$, $V = 13.36 \text{ cm}^3/\text{g}$.

$P_c = 3.648 \text{ MPa}$, $T_c = 408.14 \text{ K}$, $\omega = 0.177$, $MW = 58.123 \text{ g/mole}$, $R = 8.314 \text{ J/(mole}^\circ\text{K)}$.

Compressibility charts and the Peng-Robinson equation are given below.

(7.06) N. B. Vargaftik lists the following experimental data...

P	Pr	Z(0)	Z(0.25)	Z(0.177)	Exp V	Gen Chart V=ZRT/P*MW	% Deviation	PREOS	
								V (PR)	% Deviation
1.013	0.278	0.9	0.92	0.91416	60.7	57.97198837	4.4942531	58.25066	4.0351645
2.026	0.555	0.85	0.85	0.85	27.79	26.95162232	3.0168323	26.37752	5.0827015
3.546	0.972	0.68	0.7	0.69416	13.36	12.57730296	5.8585108	12.47146	6.6507201
7.091	1.944	0.4	0.42	0.41416	3.818	3.752028201	1.7279151	3.832948	0.3915211