# CH365 Chemical Engineering Thermodynamics

## Lesson 14

## Generalized Correlations for Gases and Liquids

Professor Andrew Biaglow
21 September 2022

# Generalized Correlations for Gases

## Lee-Kesler Method

Byung Ik Lee and Michael Kesler,
AIChE Journal, 1975, 21(3), 511-527

### Pitzer Correlation

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

(Eq. 3.53)

simple fluids

deviation from simple fluids:

$$\omega Z^1 = Z - Z^0$$

$$Z^0 = 1 + B^0 \frac{P_r}{T_r} \qquad Z^1 = B^1 \cdot \frac{P_r}{T_r}$$

(Eq. 3.60)

Lesson 13, Slide 5
formulas for $B^0$ and $B^1$
eqns. 3.61 and 3.62

---

### Lee-Kesler Modification

$Z^{(r)}$: calculated for n-octane

$$Z = Z^0 + \frac{\omega}{\omega^{(r)}}\left(Z^{(r)} - Z^0\right)$$

where

$$Z^1 = \frac{\left(Z^{(r)} - Z^0\right)}{\omega^{(r)}}$$

Lee and Kesler used a modified Benedict-Webb-Rubin EOS:

$$Z = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^5} + \frac{c_4}{T_r^3 V_r^2}\left(\beta + \frac{\gamma}{V_r^2}\right)\exp\left(-\frac{\gamma}{V_r^2}\right)$$

B, C, D are functions of $T_r$
(published in the paper)
$\beta$, $\gamma$, $c_4$, etc. are constants

Z calculated twice:
$Z^0$: calculated for simple fluids
$Z^{(r)}$: calculated for n-octane

**(Gases)**

# Lee-Kesler Method

Tables: Appendix – Tables D.1-D.4, pp. 676-692

Example: Find Z for n-octane at $P_r$=0.4, $T_r$=0.9

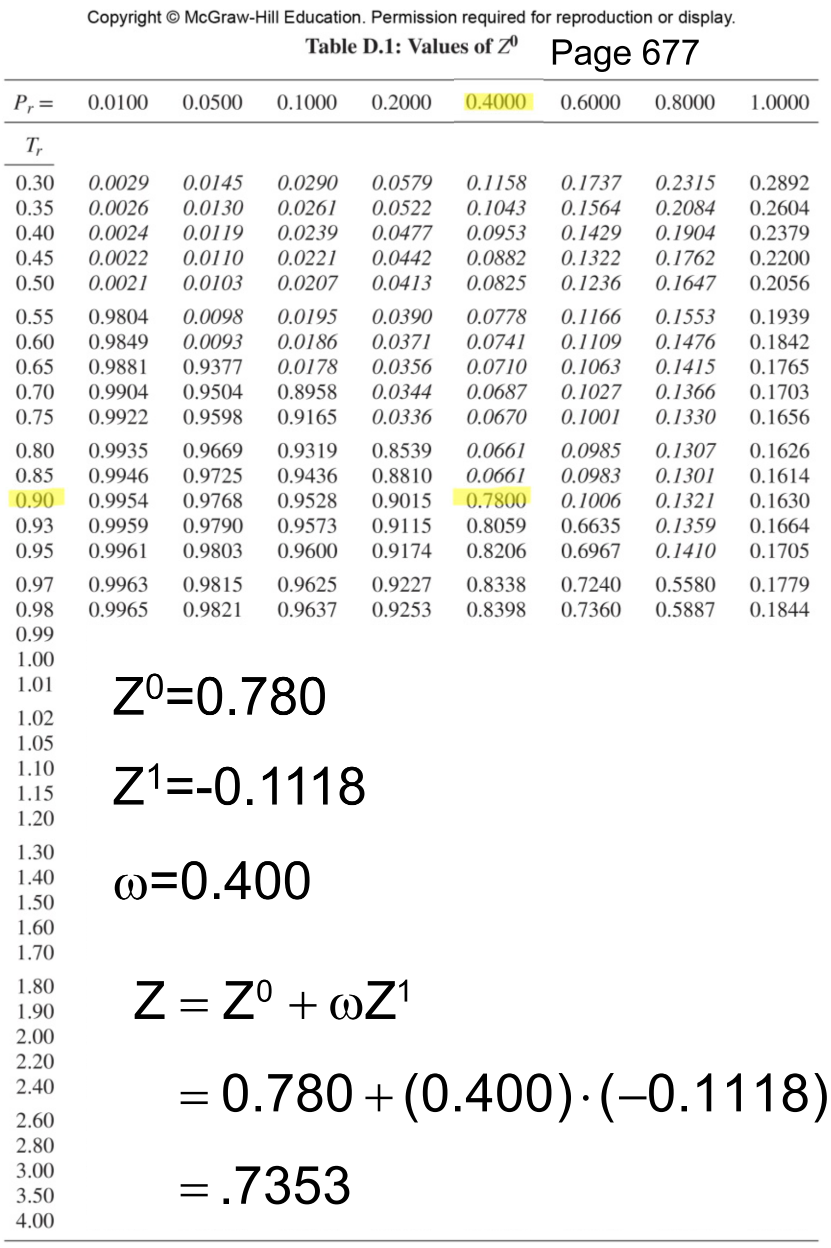


**Table D.1: Values of $Z^0$** Page 677

| $P_r =$ $T_r$ | 0.0100 | 0.0500 | 0.1000 | 0.2000 | 0.4000 | 0.6000 | 0.8000 | 1.0000 |
|---|---|---|---|---|---|---|---|---|
| 0.30 | *0.0029* | *0.0145* | *0.0290* | *0.0579* | *0.1158* | *0.1737* | *0.2315* | 0.2892 |
| 0.35 | *0.0026* | *0.0130* | *0.0261* | *0.0522* | *0.1043* | *0.1564* | *0.2084* | 0.2604 |
| 0.40 | *0.0024* | *0.0119* | *0.0239* | *0.0477* | *0.0953* | *0.1429* | *0.1904* | 0.2379 |
| 0.45 | *0.0022* | *0.0110* | *0.0221* | *0.0442* | *0.0882* | *0.1322* | *0.1762* | 0.2200 |
| 0.50 | *0.0021* | *0.0103* | *0.0207* | *0.0413* | *0.0825* | *0.1236* | *0.1647* | 0.2056 |
| 0.55 | 0.9804 | *0.0098* | *0.0195* | *0.0390* | *0.0778* | *0.1166* | *0.1553* | 0.1939 |
| 0.60 | 0.9849 | *0.0093* | *0.0186* | *0.0371* | *0.0741* | *0.1109* | *0.1476* | 0.1842 |
| 0.65 | 0.9881 | 0.9377 | *0.0178* | *0.0356* | *0.0710* | *0.1063* | *0.1415* | 0.1765 |
| 0.70 | 0.9904 | 0.9504 | 0.8958 | *0.0344* | *0.0687* | *0.1027* | *0.1366* | 0.1703 |
| 0.75 | 0.9922 | 0.9598 | 0.9165 | *0.0336* | *0.0670* | *0.1001* | *0.1330* | 0.1656 |
| 0.80 | 0.9935 | 0.9669 | 0.9319 | 0.8539 | *0.0661* | *0.0985* | *0.1307* | 0.1626 |
| 0.85 | 0.9946 | 0.9725 | 0.9436 | 0.8810 | *0.0661* | *0.0983* | *0.1301* | 0.1614 |
| 0.90 | 0.9954 | 0.9768 | 0.9528 | 0.9015 | 0.7800 | *0.1006* | *0.1321* | 0.1630 |
| 0.93 | 0.9959 | 0.9790 | 0.9573 | 0.9115 | 0.8059 | 0.6635 | *0.1359* | 0.1664 |
| 0.95 | 0.9961 | 0.9803 | 0.9600 | 0.9174 | 0.8206 | 0.6967 | *0.1410* | 0.1705 |
| 0.97 | 0.9963 | 0.9815 | 0.9625 | 0.9227 | 0.8338 | 0.7240 | 0.5580 | 0.1779 |
| 0.98 | 0.9965 | 0.9821 | 0.9637 | 0.9253 | 0.8398 | 0.7360 | 0.5887 | 0.1844 |
| 0.99 | | | | | | | | |
| 1.00 | | | | | | | | |
| 1.01 | | | | | | | | |
| 1.02 | | | | | | | | |
| 1.05 | | | | | | | | |
| 1.10 | | | | | | | | |
| 1.15 | | | | | | | | |
| 1.20 | | | | | | | | |
| 1.30 | | | | | | | | |
| 1.40 | | | | | | | | |
| 1.50 | | | | | | | | |
| 1.60 | | | | | | | | |
| 1.70 | | | | | | | | |
| 1.80 | | | | | | | | |
| 1.90 | | | | | | | | |
| 2.00 | | | | | | | | |
| 2.20 | | | | | | | | |
| 2.40 | | | | | | | | |
| 2.60 | | | | | | | | |
| 2.80 | | | | | | | | |
| 3.00 | | | | | | | | |
| 3.50 | | | | | | | | |
| 4.00 | | | | | | | | |

$Z^0$=0.780

$Z^1$=-0.1118

$\omega$=0.400

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

$$= 0.780 + (0.400)\cdot(-0.1118)$$

$$= .7353$$

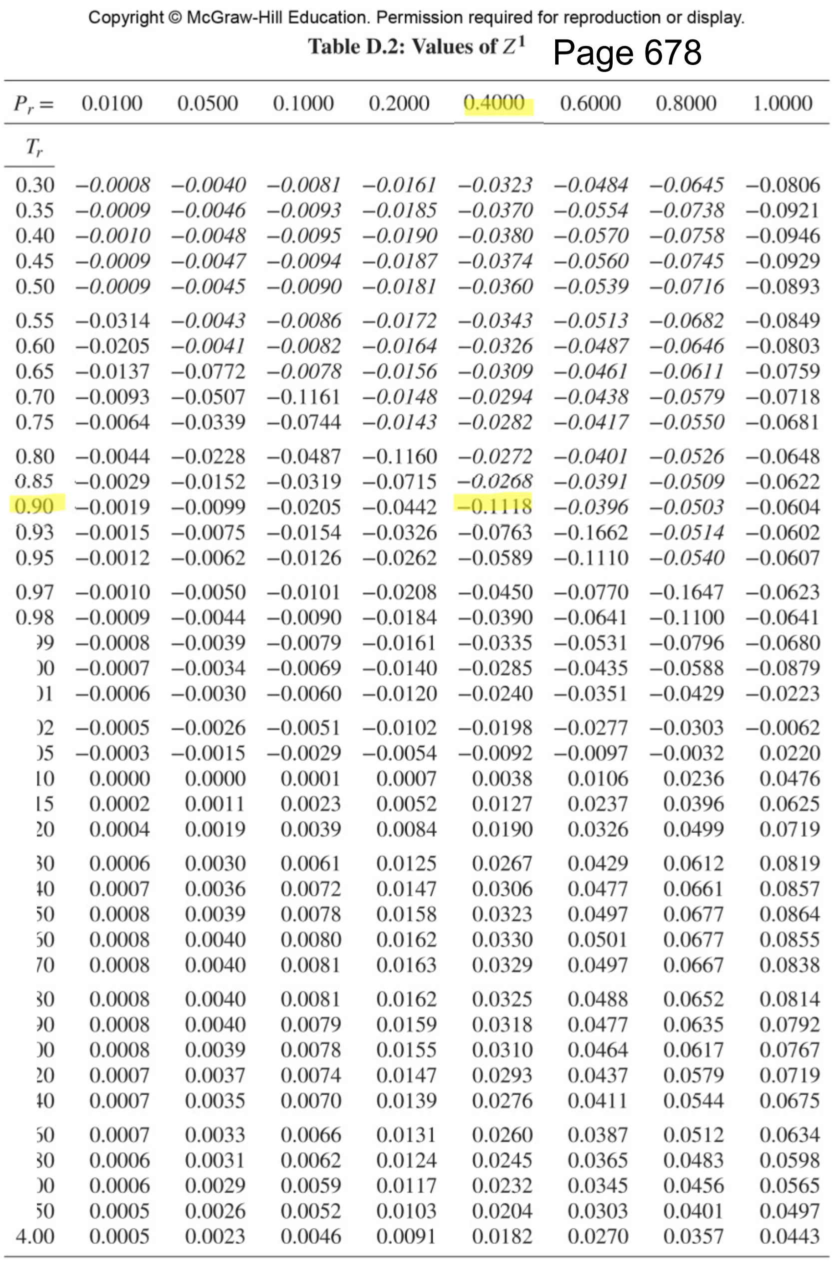


**Table D.2: Values of $Z^1$** Page 678

| $P_r =$ $T_r$ | 0.0100 | 0.0500 | 0.1000 | 0.2000 | 0.4000 | 0.6000 | 0.8000 | 1.0000 |
|---|---|---|---|---|---|---|---|---|
| 0.30 | *−0.0008* | *−0.0040* | *−0.0081* | *−0.0161* | *−0.0323* | *−0.0484* | *−0.0645* | −0.0806 |
| 0.35 | *−0.0009* | *−0.0046* | *−0.0093* | *−0.0185* | *−0.0370* | *−0.0554* | *−0.0738* | −0.0921 |
| 0.40 | *−0.0010* | *−0.0048* | *−0.0095* | *−0.0190* | *−0.0380* | *−0.0570* | *−0.0758* | −0.0946 |
| 0.45 | *−0.0009* | *−0.0047* | *−0.0094* | *−0.0187* | *−0.0374* | *−0.0560* | *−0.0745* | −0.0929 |
| 0.50 | *−0.0009* | *−0.0045* | *−0.0090* | *−0.0181* | *−0.0360* | *−0.0539* | *−0.0716* | −0.0893 |
| 0.55 | −0.0314 | *−0.0043* | *−0.0086* | *−0.0172* | *−0.0343* | *−0.0513* | *−0.0682* | −0.0849 |
| 0.60 | −0.0205 | *−0.0041* | *−0.0082* | *−0.0164* | *−0.0326* | *−0.0487* | *−0.0646* | −0.0803 |
| 0.65 | −0.0137 | −0.0772 | *−0.0078* | *−0.0156* | *−0.0309* | *−0.0461* | *−0.0611* | −0.0759 |
| 0.70 | −0.0093 | −0.0507 | −0.1161 | *−0.0148* | *−0.0294* | *−0.0438* | *−0.0579* | −0.0718 |
| 0.75 | −0.0064 | −0.0339 | −0.0744 | *−0.0143* | *−0.0282* | *−0.0417* | *−0.0550* | −0.0681 |
| 0.80 | −0.0044 | −0.0228 | −0.0487 | −0.1160 | *−0.0272* | *−0.0401* | *−0.0526* | −0.0648 |
| 0.85 | −0.0029 | −0.0152 | −0.0319 | −0.0715 | *−0.0268* | *−0.0391* | *−0.0509* | −0.0622 |
| 0.90 | −0.0019 | −0.0099 | −0.0205 | −0.0442 | −0.1118 | *−0.0396* | *−0.0503* | −0.0604 |
| 0.93 | −0.0015 | −0.0075 | −0.0154 | −0.0326 | −0.0763 | −0.1662 | *−0.0514* | −0.0602 |
| 0.95 | −0.0012 | −0.0062 | −0.0126 | −0.0262 | −0.0589 | −0.1110 | *−0.0540* | −0.0607 |
| 0.97 | −0.0010 | −0.0050 | −0.0101 | −0.0208 | −0.0450 | −0.0770 | −0.1647 | −0.0623 |
| 0.98 | −0.0009 | −0.0044 | −0.0090 | −0.0184 | −0.0390 | −0.0641 | −0.1100 | −0.0641 |
| 99 | −0.0008 | −0.0039 | −0.0079 | −0.0161 | −0.0335 | −0.0531 | −0.0796 | −0.0680 |
| 00 | −0.0007 | −0.0034 | −0.0069 | −0.0140 | −0.0285 | −0.0435 | −0.0588 | −0.0879 |
| 01 | −0.0006 | −0.0030 | −0.0060 | −0.0120 | −0.0240 | −0.0351 | −0.0429 | −0.0223 |
| 02 | −0.0005 | −0.0026 | −0.0051 | −0.0102 | −0.0198 | −0.0277 | −0.0303 | −0.0062 |
| 05 | −0.0003 | −0.0015 | −0.0029 | −0.0054 | −0.0092 | −0.0097 | −0.0032 | 0.0220 |
| 10 | 0.0000 | 0.0000 | 0.0001 | 0.0007 | 0.0038 | 0.0106 | 0.0236 | 0.0476 |
| 15 | 0.0002 | 0.0011 | 0.0023 | 0.0052 | 0.0127 | 0.0237 | 0.0396 | 0.0625 |
| 20 | 0.0004 | 0.0019 | 0.0039 | 0.0084 | 0.0190 | 0.0326 | 0.0499 | 0.0719 |
| 30 | 0.0006 | 0.0030 | 0.0061 | 0.0125 | 0.0267 | 0.0429 | 0.0612 | 0.0819 |
| 40 | 0.0007 | 0.0036 | 0.0072 | 0.0147 | 0.0306 | 0.0477 | 0.0661 | 0.0857 |
| 50 | 0.0008 | 0.0039 | 0.0078 | 0.0158 | 0.0323 | 0.0497 | 0.0677 | 0.0864 |
| 50 | 0.0008 | 0.0040 | 0.0080 | 0.0162 | 0.0330 | 0.0501 | 0.0677 | 0.0855 |
| 70 | 0.0008 | 0.0040 | 0.0081 | 0.0163 | 0.0329 | 0.0497 | 0.0667 | 0.0838 |
| 30 | 0.0008 | 0.0040 | 0.0081 | 0.0162 | 0.0325 | 0.0488 | 0.0652 | 0.0814 |
| 90 | 0.0008 | 0.0040 | 0.0079 | 0.0159 | 0.0318 | 0.0477 | 0.0635 | 0.0792 |
| 00 | 0.0008 | 0.0039 | 0.0078 | 0.0155 | 0.0310 | 0.0464 | 0.0617 | 0.0767 |
| 20 | 0.0007 | 0.0037 | 0.0074 | 0.0147 | 0.0293 | 0.0437 | 0.0579 | 0.0719 |
| 40 | 0.0007 | 0.0035 | 0.0070 | 0.0139 | 0.0276 | 0.0411 | 0.0544 | 0.0675 |
| 50 | 0.0007 | 0.0033 | 0.0066 | 0.0131 | 0.0260 | 0.0387 | 0.0512 | 0.0634 |
| 30 | 0.0006 | 0.0031 | 0.0062 | 0.0124 | 0.0245 | 0.0365 | 0.0483 | 0.0598 |
| 00 | 0.0006 | 0.0029 | 0.0059 | 0.0117 | 0.0232 | 0.0345 | 0.0456 | 0.0565 |
| 50 | 0.0005 | 0.0026 | 0.0052 | 0.0103 | 0.0204 | 0.0303 | 0.0401 | 0.0497 |
| 4.00 | 0.0005 | 0.0023 | 0.0046 | 0.0091 | 0.0182 | 0.0270 | 0.0357 | 0.0443 |

# Generalized Correlations for Liquids

Rackett: $V^{sat} = V_C Z_C^{(1-T_r)^{2/7}}$ (Eq. 3.68) $Z^{sat} = \frac{P_r}{T_r} Z_C^{\left[1+(1-T_r)^{2/7}\right]}$ (Eq. 3.69)

$\rho_r = 2.47$

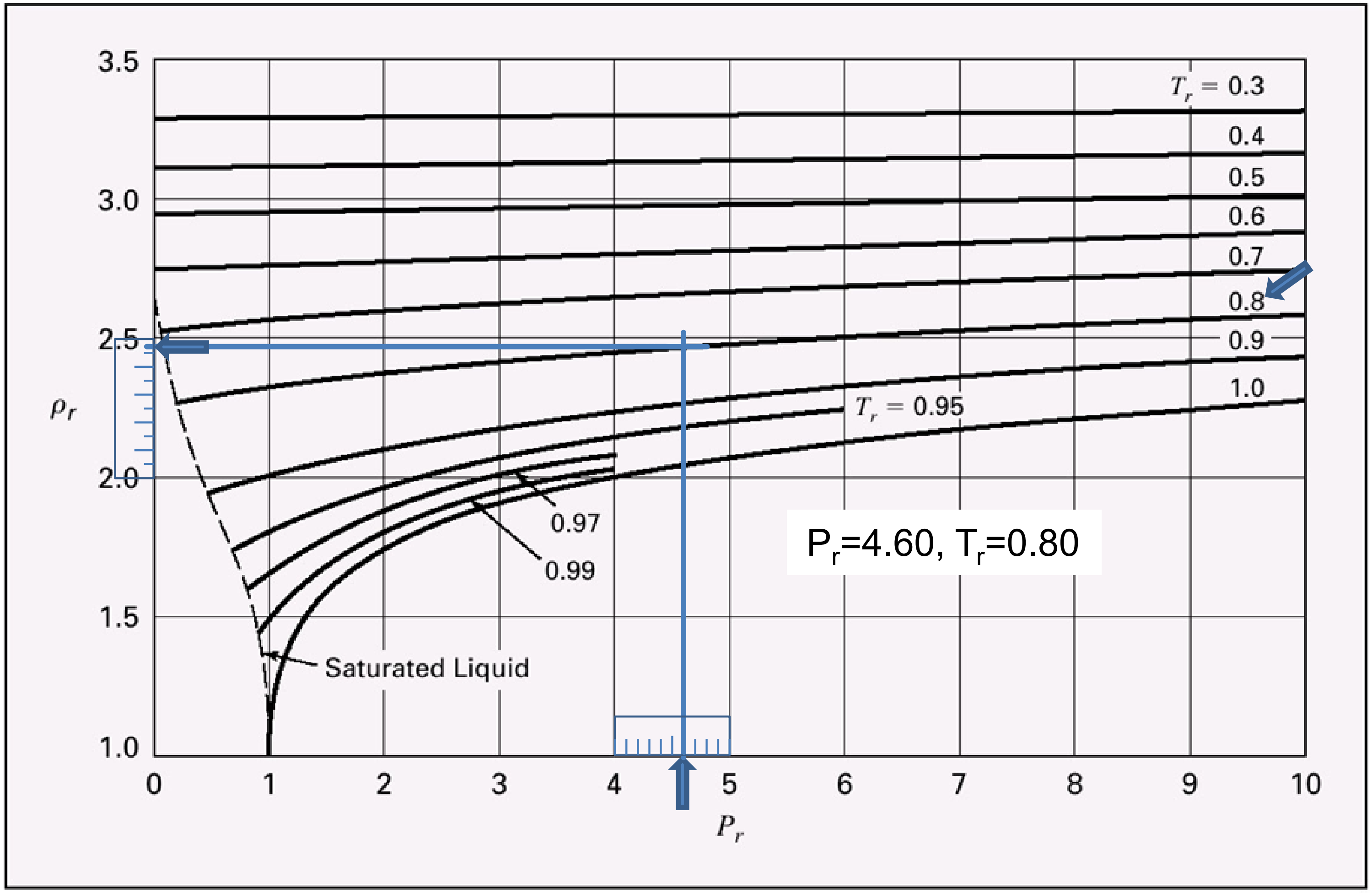


**Figure 3.15:** Generalized density correlation for liquids.

Lydersen, Greenkorn, and Hougen: $\rho_r \equiv \frac{\rho}{\rho_C} = \frac{V_C}{V}$ (Eq. 3.70)

**(Liquids)**

# Example 3.14

For ammonia at 310 K, estimate the molar volume ~~density~~ of (a) the saturated liquid and (b) the liquid at 100 bar.

experimental:

$$V^{sat} = 29.14\,\frac{cm^3}{mol}$$

Part (a) Use Table B.1, Appendix B, pp. 663-665:

(B.1, 665) $T_C = 405.7\,K \Rightarrow T_r = \frac{310}{405.7} = 0.7641$

(B.1, 665) $V_C = 72.5\,\frac{cm^3}{mol}$

(B.1, 665) $Z_C = 0.242$

(Eq. 3.68, Rackett)

$$\Rightarrow V^{sat} = V_C Z_C^{(1-T_r)^{2/7}} = 72.5 \cdot 0.242^{(1-0.7641)^{2/7}} = \underline{\underline{28.35\,\frac{cm^3}{mol}}}$$

ANS

Part (b)

(B.1, 665) $P_C = 112.8\,bar \Rightarrow P_r = \frac{100}{112.8} = 0.8865 \Rightarrow$ $T_r = 0.7641$, $P_r = 0.8865$

$\Rightarrow$ Now use Fig. 3.15 for $\rho_r$ then eq. 3.70 for molar volume

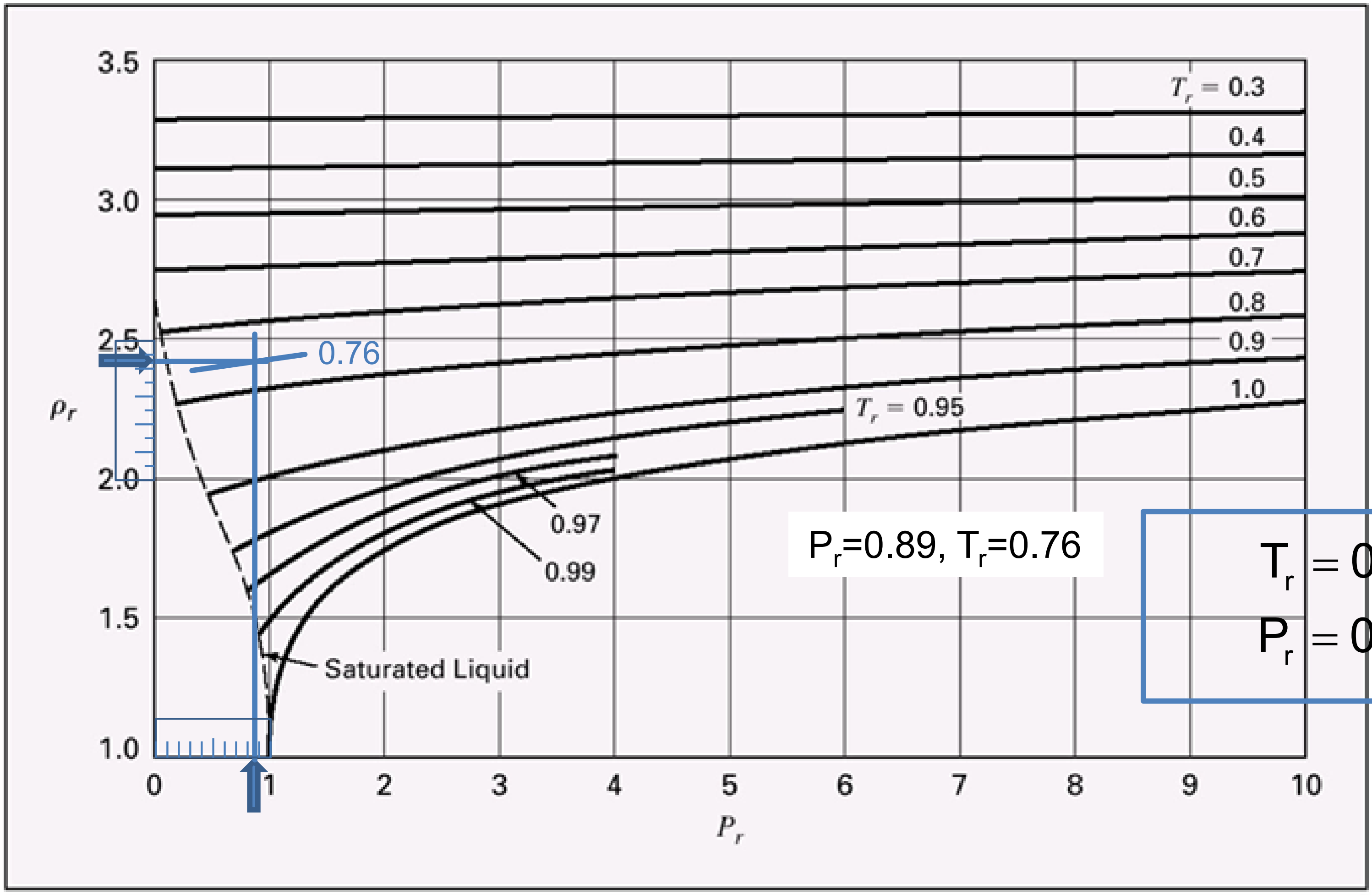
**(Liquids)**

# Example 3.14 , part b, continued

Rackett: $V^{sat} = V_C Z_C^{(1-T_r)^{2/7}}$ (Eq. 3.68) $Z^{sat} = \frac{P_r}{T_r} Z_C^{\left[1+(1-T_r)^{2/7}\right]}$ (Eq. 3.69)

$\rho_r = 2.43$

solution deviates from book; authors read reduced density as 2.38 on p. 117



$P_r$=0.89, $T_r$=0.76

**Figure 3.15.** Generalized density correlation for liquids.

$T_r = 0.7641$

$P_r = 0.8865$

Lydersen, Greenkorn, and Hougen: $\rho_r \equiv \frac{\rho}{\rho_C} = \frac{V_C}{V}$ (Eq. 3.70)

**(Liquids)**

# Example 3.14, continued

For ammonia at 310 K, estimate the molar volume ~~density~~ of (a) the saturated liquid and (b) the liquid at 100 bar.

experimental:

$$V^{sat} = 29.14\,\frac{cm^3}{mol}$$

Part (a) Use Table B.1, Appendix B, pp. 663-665:

(B.1, 665) $T_C = 405.7\,K \Rightarrow T_r = \frac{310}{405.7} = 0.7641$

(B.1, 665) $V_C = 72.5\,\frac{cm^3}{mol}$

(B.1, 665) $Z_C = 0.242$

(Eq. 3.68, Rackett)

$$\left.\begin{matrix} V_C \\ Z_C \end{matrix}\right\} \Rightarrow V^{sat} = V_C Z_C^{(1-T_r)^{2/7}} = 72.5 \cdot 0.242^{(1-0.7641)^{2/7}} = \underline{\underline{28.35\,\frac{cm^3}{mol}}}$$

ANS

Part (b)

$$P_C = 112.8\,bar \Rightarrow P_r = \frac{100}{112.8} = 0.8865 \Rightarrow \rho_r = 2.4$$

Use Fig. 3.15

$$\rho_r \equiv \frac{\rho}{\rho_C} = \frac{V_C}{V} \Rightarrow V = \frac{V_C}{\rho_r} \Rightarrow V = \frac{72.5}{2.43} = \underline{\underline{29.8\,\frac{cm^3}{mol}}}$$

(Eq. 3.70)

$\rho_r$ = 2.43 from slide 6, Figure 3.15

ANS

# Homework

# Problem 3.58

To a good approximation, what is the molar volume of ethanol vapor at 480 deg C and 6000 kPa? How does this result compare with the ideal gas?

Answer the problem in four parts:

(a) Lee-Kesler method.

(b) SRK equation.

(c) Ideal gas equation.

For comparison: Compare LK and SRK to IG. If either is less than IG, explain why using knowledge of IG behavior.

Online Interpolator Tool for Lee-Kesler Tables:
https://www.ajdesigner.com/phpinterpolation/bilinear_interpolation_equation.php