CH365 Chemical Engineering Thermodynamics

Lesson 14

Generalized Correlations for Gases and Liquids

Generalized Correlations for Gases
Lee-Kesler Method

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

Pitzer Correlation (L13)

$$Z = Z^0 + \omega Z^1$$ (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)
β, γ, 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

ω=0.400

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

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

$$= .7353$$

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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
)9	−0.0008	−0.0039	−0.0079	−0.0161	−0.0335	−0.0531	−0.0796	−0.0680
)0	−0.0007	−0.0034	−0.0069	−0.0140	−0.0285	−0.0435	−0.0588	−0.0879
)1	−0.0006	−0.0030	−0.0060	−0.0120	−0.0240	−0.0351	−0.0429	−0.0223
)2	−0.0005	−0.0026	−0.0051	−0.0102	−0.0198	−0.0277	−0.0303	−0.0062
)5	−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
)0	0.0008	0.0040	0.0079	0.0159	0.0318	0.0477	0.0635	0.0792
)0	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
)0	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)

$\rho_r = 2.47$

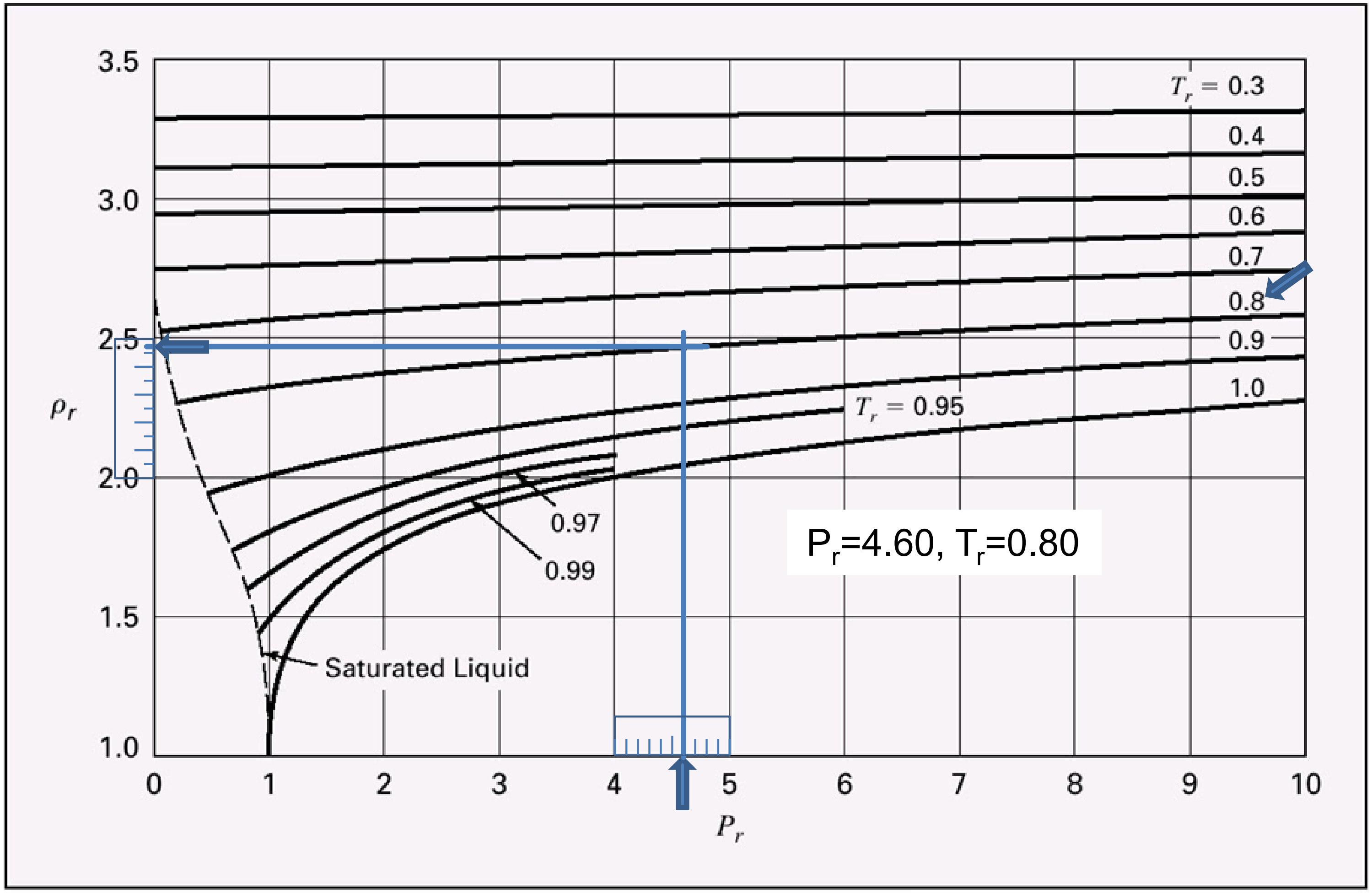

Figure 3.15: Generalized density correlation for liquids.

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

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.

(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

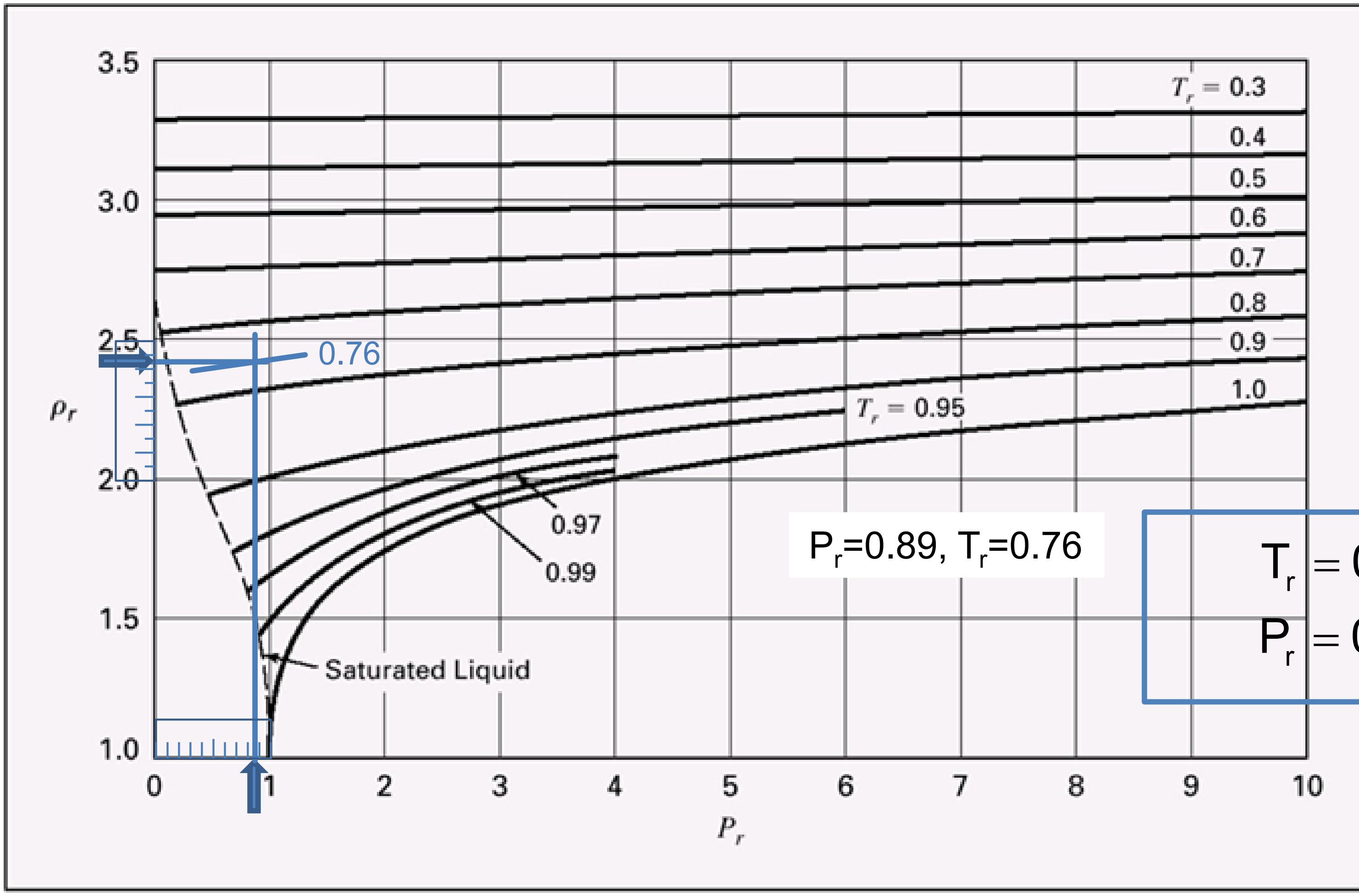

Figure 3.15. Generalized density correlation for liquids.

$T_r = 0.7641$
$P_r = 0.8865$

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

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.

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