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)

$$Z = Z^0 + \omega Z^1 \quad \text{(Eq. 3.53)}$$

simple fluids

deviation from simple fluids:

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

$$Z^0 = 1 + B^0 \frac{P_r}{T_r} \qquad Z^1 = B^1 \cdot \frac{P_r}{T_r} \quad \text{(Eq. 3.60)}$$

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

<u>Z calculated twice</u>:
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

$P_r =$	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
T_r								
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

$P_r =$	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
T_r								
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
60	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
80	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
60	0.0007	0.0033	0.0066	0.0131	0.0260	0.0387	0.0512	0.0634
80	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)

$\rho_r = 2.47$

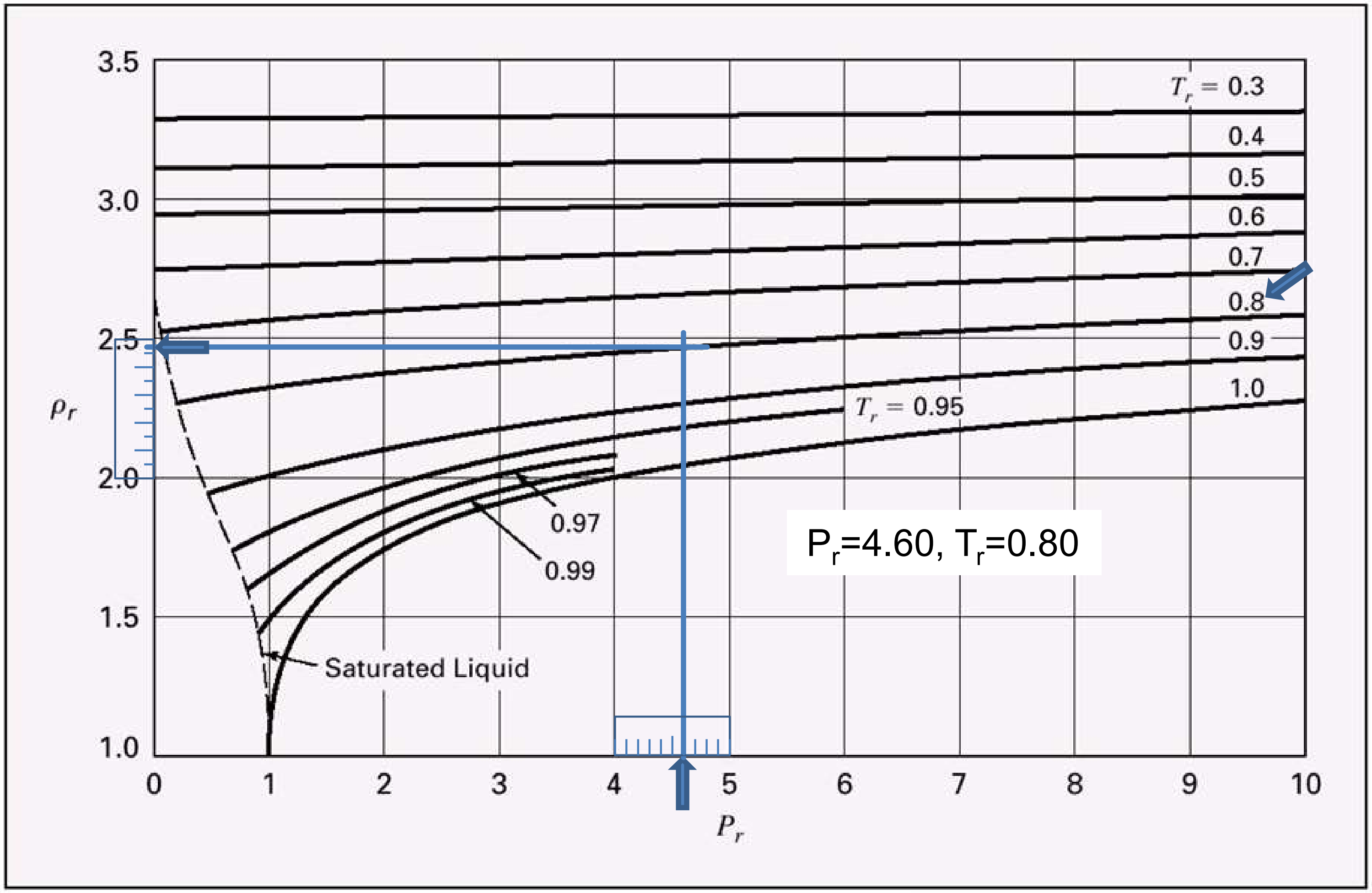

Figure 3.15: Generalized density correlation for liquids.

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

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

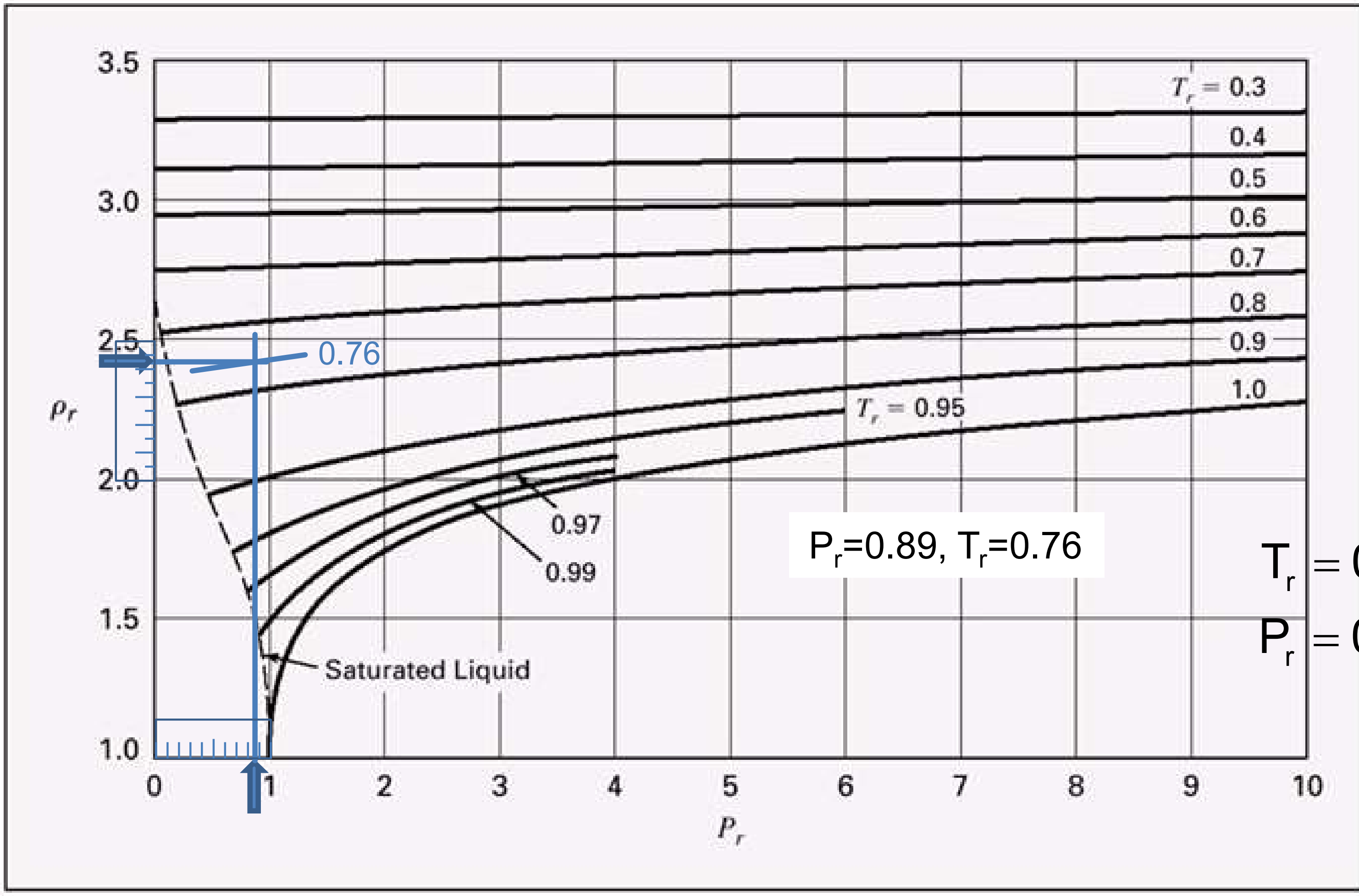

Figure 3.15. Generalized density correlation for liquids.

$T_r = 0.7641$

$P_r = 0.8865$

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.

Questions