

ENGG 201

What is Going On with Real Gases (A Brief Outline of What is Important in Ch 6)

Chapter 6 – Real Gases

Main Concepts:

1. Pure Real Gases (Sections 6.1-6.7)
 - a. How are the VOLUME, TEMPERATURE and PRESSURE related for Real Gases?
2. Real Gas Mixtures (Section 6.8)
 - a. How are the VOLUME, TEMPERATURE and PRESSURE related for Mixtures of Real Gases?

Things to Remember:

Pure Real Gases

1. van der Waals equation of State (vdW EOS)

- a. Two Forms:

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad \text{OR} \quad V_m^3 - \left[b + \frac{RT}{P}\right]V_m^2 + \frac{a}{P}V_m - \frac{ab}{P} = 0$$

- b. Get a, b from T_c and P_c (and the reverse)

$$P_c = \frac{a}{27b^2} \quad T_c = \frac{8a}{27Rb} \quad V_c = 3b$$

$$a = \frac{27}{64} \frac{R^2 T_c^2}{P_c} \quad b = \frac{RT_c}{8P_c}$$

2. Corresponding States

$$PV_m = ZRT \quad T_r = \frac{T}{T_c} \quad P_r = \frac{P}{P_c}$$

- a. Z from Generalized Compressibility Charts
- b. Z from Pitzer Curl Tables (need ω) and then: $Z = Z^{(0)} + \omega Z^{(1)}$

Mixtures of Real Gases

3. van der Waals equation of State $a = [\sum y_i \sqrt{a_i}]^2$ and $b = \sum y_i b_i$ and then use vdW as you would for a pure gas
4. Pseudo-critical Method (Kay's Method). $T_{pc} = \sum_i y_i T_{ci}$, $P_{pc} = \sum_i y_i P_{ci}$ and then look up Z (chart or Pitzer-Curl tables) as you would for a pure gas
5. Watch units – pay attention to R.
6. Trial and error when solving for V in vdW – use ideal gas as a first guess.
 - a. Vapor volume is largest of 3 positive roots ($T < T_c$).
 - b. Gas volume is only positive root ($T > T_c$).
 - c. Critical volume = all 3 real positive roots are equal ($T = T_c$).
7. Write out a table for vdW Mixing Rules.

Examples of Typical Problems:

Pure Gases and/or Mixtures of Real Gases

1. Given P, T, calculate V.
2. After calculating V, may have to further calculate dimensions of container or mass/moles of substance in container.
3. Given V, T, calculate P.
4. More ... (See old finals).

GENERALIZED COMPRESSIBILITY FACTORS
($Z_c = 0.27$)

This chart plots the compressibility factor (z) on the y-axis (ranging from 0 to 1.5) against the reduced pressure (P_r) on the x-axis (logarithmic scale from 0.1 to 30). The chart is divided into two regions by a vertical line at $P_r = 1.0$. The left region ($P_r < 1.0$) shows the behavior of saturated gases and liquids, with curves for reduced temperatures (T_r) ranging from 0.80 to 1.00. The right region ($P_r > 1.0$) shows the behavior of supercritical fluids, with curves for T_r ranging from 1.00 to 1.50. The curves generally show that z decreases as P_r increases, and the effect of T_r is more pronounced at lower pressures.

PITZER-CURL TABLES

Table C-1
Pitzer-Curl Generalized $Z^{(0)}$

Tr	0.2	0.4	0.6	0.8	1.0	1.2	1.4	Pr 1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0
0.80	0.851	0.066	0.100	0.133	0.164	0.192	0.255	0.258	0.287	0.318	0.347	0.376	0.405	0.433	0.461
0.85	0.882	0.067	0.101	0.134	0.165	0.194	0.226	0.258	0.287	0.316	0.345	0.374	0.403	0.431	0.459
0.90	0.904	0.778	0.102	0.135	0.167	0.198	0.229	0.258	0.288	0.316	0.345	0.373	0.402	0.430	0.458
0.95	0.920	0.819	0.697	0.145	0.176	0.205	0.235	0.262	0.292	0.321	0.347	0.375	0.403	0.430	0.457
1.00	0.932	0.849	0.756	0.638	0.291	0.231	0.250	0.278	0.304	0.329	0.356	0.381	0.407	0.433	0.458
1.05	0.942	0.874	0.800	0.714	0.609	0.470	0.341	0.320	0.332	0.350	0.372	0.393	0.417	0.441	0.446
1.10	0.950	0.893	0.833	0.767	0.691	0.607	0.512	0.442	0.408	0.402	0.405	0.420	0.440	0.462	0.484
1.15	0.958	0.98	0.858	0.805	0.746	0.684	0.620	0.562	0.514	0.484	0.477	0.478	0.485	0.498	0.513
1.20	0.963	0.921	0.879	0.835	0.788	0.737	0.690	0.640	0.598	0.568	0.553	0.545	0.544	0.548	0.554
1.25	0.968	0.930	0.896	0.858	0.820	0.778	0.740	0.702	0.664	0.636	0.618	0.606	0.599	0.597	0.598
1.30	0.971	0.940	0.909	0.878	0.846	0.811	0.780	0.749	0.718	0.691	0.671	0.657	0.649	0.644	0.642
1.4	0.977	0.952	0.929	0.908	0.883	0.859	0.838	0.817	0.795	0.777	0.759	0.745	0.734	0.725	0.720
1.5	0.982	0.963	0.945	0.927	0.909	0.892	0.875	0.859	0.844	0.831	0.819	0.808	0.800	0.794	0.790
1.6	0.985	0.971	0.957	0.944	0.930	0.917	0.904	0.893	0.882	0.872	0.863	0.855	0.848	0.843	0.840
1.7	0.988	0.977	0.966	0.956	0.946	0.936	0.926	0.919	0.911	0.903	0.896	0.889	0.889	0.883	0.879
1.8	0.991	0.982	0.974	0.966	0.958	0.950	0.944	0.937	0.931	0.926	0.921	0.916	0.913	0.910	0.908
1.9	0.993	0.986	0.980	0.974	0.968	0.962	0.958	0.952	0.948	0.944	0.940	0.936	0.933	0.931	0.930
2.0	0.995	0.989	0.984	0.979	0.975	0.971	0.968	0.964	0.961	0.959	0.956	0.954	0.953	0.953	0.952

Table C-2
Pitzer-Curl Generalized $Z^{(1)}$

Tr	0.2	0.4	0.6	0.8	1.0	1.2	1.4	Pr 1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0
0.80	-0.095	-0.028	-0.044	-0.058	-0.07	-0.08	-0.10	-0.11	-0.12	-0.13	-0.14	-0.15	-0.16	-0.17	-0.18
0.85	-0.067	-0.031	-0.049	-0.064	-0.08	-0.09	-0.11	-0.12	-0.13	-0.14	-0.15	-0.16	-0.17	-0.18	-0.18
0.90	-0.042	-0.09	-0.053	-0.068	-0.085	-0.10	-0.11	-0.12	-0.13	-0.14	-0.15	-0.16	-0.17	-0.17	-0.18
0.95	-0.025	-0.050	-0.100	-0.072	-0.091	-0.10	-0.11	-0.12	-0.12	-0.13	-0.14	-0.15	-0.15	-0.16	-0.17
1.00	-0.012	-0.16	-0.20	-0.05	-0.080	-0.090	-0.099	-0.108	-0.115	-0.123	-0.13	-0.13	-0.14	-0.14	-0.15
1.05	0.000	+0.001	+0.005	+0.015	+0.02	+0.01	-0.01	-0.04	-0.06	-0.07	-0.08	-0.09	-0.10	-0.11	
1.10	+0.002	0.008	0.016	0.030	0.055	0.082	+0.11	+0.082	+0.035	0.000	-0.02	-0.03	-0.05	-0.06	-0.07
1.15	0.004	0.012	0.012	0.040	0.064	0.093	0.12	0.140	0.136	+0.100	+0.07	+0.04	+0.02	0.00	-0.01
1.20	0.009	0.018	0.028	0.044	0.069	0.10	0.13	0.16	0.17	0.17	0.16	0.14	0.12	+0.09	+0.07
1.25	0.011	0.023	0.036	0.050	0.069	0.10	0.13	0.16	0.18	0.19	0.19	0.18	0.16	0.14	0.12
1.30	0.013	0.027	0.041	0.055	0.072	0.10	0.13	0.16	0.18	0.20	0.20	0.20	0.20	0.19	0.18
1.4	0.016	0.032	0.049	0.065	0.082	0.10	0.13	0.16	0.18	0.19	0.20	0.21	0.21	0.21	0.20
1.5	0.017	0.035	0.052	0.070	0.088	0.10	0.13	0.15	0.17	0.18	0.20	0.20	0.21	0.21	0.21
1.6	0.018	0.036	0.054	0.07	0.08	0.10	0.12	0.14	0.16	0.17	0.18	0.19	0.20	0.20	0.21
1.7	0.018	0.036	0.054	0.07	0.09	0.10	0.11	0.13	0.15	0.16	0.17	0.18	0.19	0.20	0.21
1.8	0.018	0.036	0.054	0.07	0.09	0.10	0.11	0.13	0.15	0.16	0.17	0.18	0.19	0.20	0.21
1.9	0.018	0.035	0.05	0.07	0.09	0.10	0.11	0.13	0.15	0.16	0.17	0.18	0.19	0.20	0.21
2.0	0.016	0.031	0.05	0.07	0.08	0.10	0.11	0.13	0.14	0.15	0.16	0.17	0.19	0.20	0.21