**Generalization correlations of gases**

Equations of state that express $Z$ as function of $T_r$ and $P_r$ are said to be generalized because of their applicability for all gases, and an alternative to the use of an equation is a graph $Z$ vs. $P_r$.

→ Generalized chart can be prepared from generalized equation
→ Alternatively, the isotherms may be drawn to provide the best fit to experimental PVT data for various gases
→ Advantages of generalized correlation is that allow to prediction of property values from very limited information.

**1-Pitzer Correlations for the Compressibility Factor**

Experimental observations shows $Z = f(T_r, P_r)$ for different fluids, and this is the basis for the two-parameter theorem of corresponding states:

*All fluids, when compared at the same reduced temperature and reduced pressure, have approximately the same compressibility factor, and all deviate from ideal-gas behavior to about the same degree.*

Although this theorem is very nearly exact for the simple fluids (Ar, Kr, and Xe) systematic deviations are observed for more complex fluids. Appreciable improvement results from introduction of a third corresponding-states parameter, characteristic of molecular structure.

The definition of $\omega$ makes its value zero for argon, krypton, and xenon, and experimental data yield compressibility factors for all three fluids that are correlated by the same curves when $Z$ is represented as a function of $T_r$ and $P_r$. This is the basic premise of the following three-parameter theorem of corresponding states:

*All fluids having the same value of $\omega$, when compared at the same $T_r$ and $P_r$ have about the same value of $Z$, and all deviate from ideal-gas behavior to about the same degree.*

the most popular such parameter is the acentric factor $\omega$, introduced by K. S. Pitzer and coworkers. Where $\omega$ for pure chemical species defined with reference to its vapor pressure
Pitzer noted that all vapor-pressure data for the simple fluids (Ar, Kr, Xe) lie on the same line when plotted as log \( P_{r,\text{Sat}} \) vs. \( \frac{1}{T_r} \) and that the line passes through log \( P_{r,\text{Sat}} = -1.0 \) at \( T_r = 0.7 \).

\[
\log P_{r,\text{Sat}} = a - \frac{b}{T_r}
\]

represent a straight line

At critical point \( T_r = P_r = 1 \)

\[
0 = a - \frac{b}{1} \Rightarrow a = b
\]

\[
\log P_r = a - \frac{a}{T_r} = a \left( 1 - \frac{1}{T_r} \right)
\]

Consider (a) a third variable and represent acentric factor \( \omega \)

Where \( \omega = -1 - \log(P_r)_{T_r=0.7} \)

And this is true for \( Z = f(T_r, P_r, \omega) \)

And this lead to \( Z = Z^o + Z^- \)

Where \( Z^o \) is the case for simple fluids and \( Z^- \) becomes identical with \( Z \).

And by use figures (3-12) and (3-13) to estimate \( Z^o \) and figures (3-14) and (3-15) to estimate \( Z^- \) (J.M. Smith, Introduction to Chemical Engineering Thermodynamics, 4th Ed., 1987 McGraw-Hill).

The uses of these figures as below

\( \rightarrow \) 3-12 for generalized correlation \( Z^o, P_r < 1.0 \)

\( \rightarrow \) 3-13 for generalized correlation \( Z^o, P_r > 1.0 \)

\( \rightarrow \) 3-14 for generalized correlation \( Z^-, P_r < 1.0 \)

\( \rightarrow \) 3-15 for generalized correlation \( Z^-, P_r < 1.0 \)
Pitzer correlation provide reliable results for gases which are nonpolar or only slightly polar; for these errors of no more than 2-3 % are indicated. A disadvantage of generalized compressibility factor correlation is its graphical nature. The simplest form of the Virial equation has validity only at low to moderate pressures where Z is linear in pressure. The generalized Virial-coefficient correlation is therefore useful only where \( Z^0 \) and \( Z' \) are at least approximately linear functions of reduced pressure.

1- Generalized Virial coefficient correlation

\[
Z = 1 + \frac{BP}{RT} = 1 + \left( \frac{BP_C}{RT_C} \right) \frac{P_r}{T_r}
\]

Pitzer and coworkers proposed a second correlation, which expressed the quantity \( \frac{BP_C}{RT_C} \), as

\[
\left( \frac{BP_C}{RT_C} \right) = B^* + B \omega'
\]

\[
Z = 1 + B^* \frac{P_r}{T_r} + \omega B' \frac{P_r}{T_r}
\]

\[
B^* = 0.083 - \frac{0.422}{T_r^{1.6}} \quad B' = 0.139 - \frac{0.172}{T_r^{4.2}}
\]