



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*:

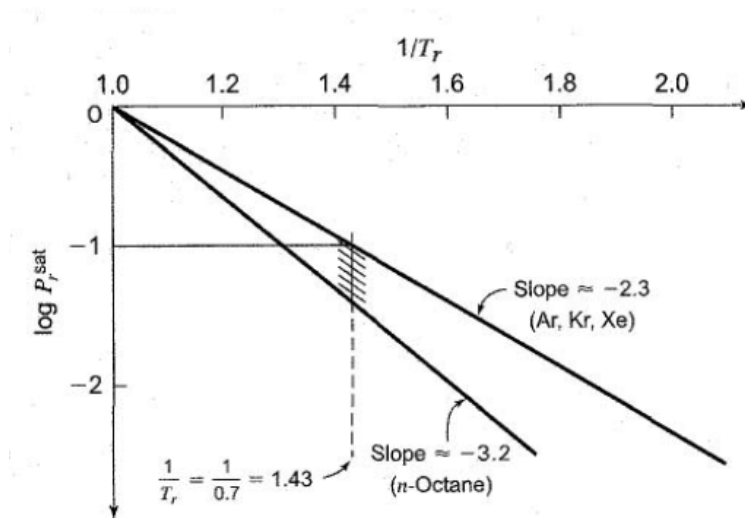
All fluids, when compared at the same reduced temperature and reduced pressure, have approximately the same compressibility factor, and all deviate from ideal-gas behavior to about the same degree.

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 ω 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 ω , 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 ω , introduced by K. S. Pitzer and coworkers. Where ω 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. $1 / T_r$ 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 ω

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 $Z = Z^\circ + Z^-$

Where Z° is the case for simple fluids and Z° becomes identical with Z .

And by use figures (3-12) and (3-13) to estimate Z° 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

- 3-12 for generalized correlation Z° , $P_r < 1.0$
- 3-13 for generalized correlation Z° , $P_r > 1.0$
- 3-14 for generalized correlation Z' , $P_r < 1.0$
- 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 BP_C/RT_C , as

$$\left(\frac{BP_C}{RT_C} \right) = B^\circ + B\omega'$$

$$Z = 1 + B^\circ \frac{P_r}{T_r} + \omega B' \frac{P_r}{T_r}$$

$$B^\circ = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$B' = 0.139 - \frac{0.172}{T_r^{4.2}}$$