

## EQUATION OF STATE

### The Ideal-Gas Equation of State

Any equation that relates the pressure, temperature, and specific volume of a substance is called an equation of state.

The simplest and best known equation of state for substances in the gas phase is the *ideal-gas equation of state*.

Gas and vapor are often used as synonymous words. The vapor phase of a substance is called a gas when it is above the critical temperature. Vapor usually implies a gas that is not far from a state of condensation.

It is experimentally observed that at a low pressure the volume of a gas is proportional to its temperature:

$$\begin{cases} P \propto T \\ P \propto \frac{1}{v} \end{cases} \rightarrow P \propto \frac{T}{v}$$

or

$$Pv = RT$$

where  $R$  is the gas constant. The above equation is called the ideal-gas equation of state (ideal gas relation). Since  $R$  is a constant for a gas, one can write:

$$R = \frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2}$$

where subscripts 1 and 2 denote two states of an ideal gas. Note that the constant  $R$  is different for each gas; see Tables A1 and A2 in Cengel book.

The ideal gas equation of state can be written in several forms:

$$\begin{cases} V = mv \rightarrow PV = mRT \\ mR = (MN)R = NR_u \rightarrow PV = N R_u T \\ V = N\bar{v} \rightarrow P\bar{v} = R_u T \end{cases}$$

where  $\bar{v}$  ( $m^3/kmol$ ) is the molar specific volume. That is the volume per unit mole.  $R_u = 8.314 \text{ kJ} / (kmol \cdot K)$  is the universal gas constant,  $R = R_u / M$ .

The molar mass  $M$ : is defined as the mass of one mole of a substance (in *gmole* or *kgmol*). The mass of a system is equal to the product of its molar mass  $M$  and the mole number  $N$ :

$$m = MN \quad (\text{kg})$$

See Table A-1 for  $R$  and  $M$  for several substances.

An ideal gas is an imaginary substance that obeys the relation  $Pv = RT$ . It is experimentally observed that the ideal gas closely approximate the  $P$ - $v$ - $T$  behavior of real gases at low densities.

In the range of practical interest, many familiar gases such as air, nitrogen, oxygen, hydrogen, helium, argon, neon, and CO<sub>2</sub> can be treated as ideal gases with negligible error.

Note: Water vapor and refrigerant vapor in refrigerators **should not** be treated as ideal gases.

Note: Water vapor at pressures below 10 kPa can be treated as an ideal gas, regardless of temperature.

### Compressibility Factor

The assumption of ideal gas relation implies that:

- The gas particles take up negligible volume
- The intermolecular potential energy between particles is small
- Particles act independent of one another

However, real gases deviate from ideal gas behavior. This deviation at given temperature and pressure can be accurately accounted for by introduction of a *correction factor* called the compressibility factor  $Z$ .

$$Z = \frac{Pv}{RT} \quad \text{or} \quad Pv = ZRT$$

or  $Z = v_{actual} / v_{ideal} \leq 1$ . Obviously,  $Z = 1$  for ideal gases.

Gases behave very much the same at temperatures and pressures normalized with respect to their critical temperatures and pressures.

$$P_R = \frac{P}{P_{cr}} \quad \text{and} \quad T_R = \frac{T}{T_{cr}}$$

Here  $P_R$  and  $T_R$  are called the *reduced pressure* and *temperature*, respectively.

By curve-fitting all the data, the general compressibility chart is obtained which can be used for all gases, see Fig. A-15.

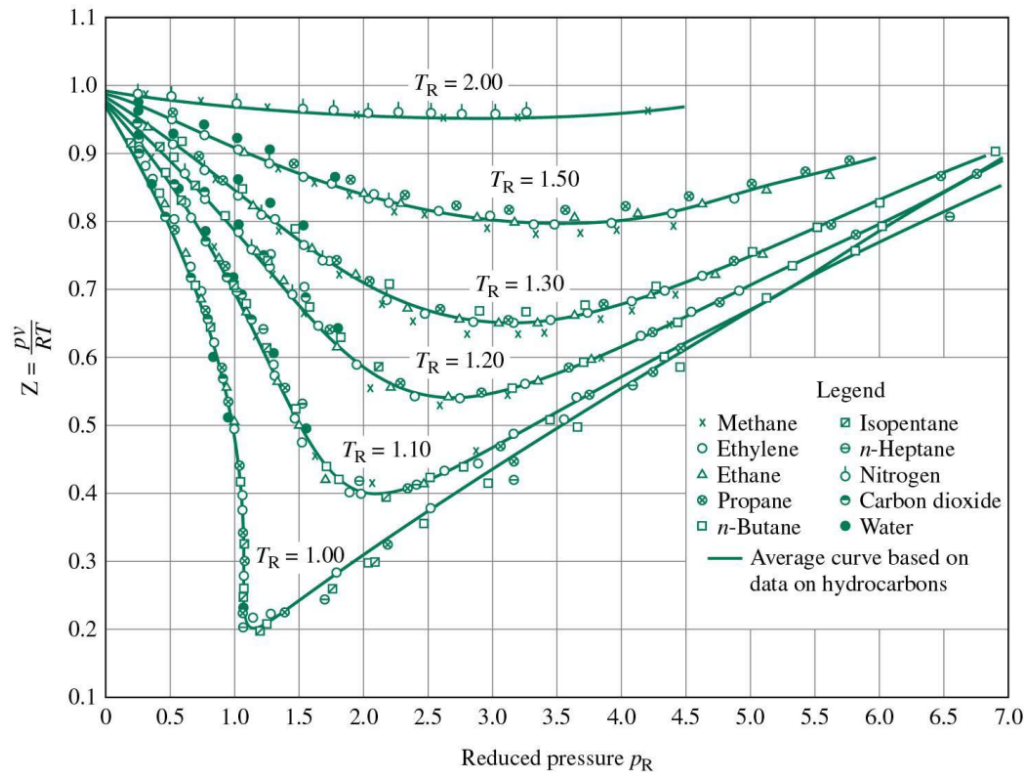


Fig. 6: Z factor, general compressibility chart.

From the Z chart, one can conclude:

- At very low pressure ( $P_R \ll 1$ ), the gases behave as an ideal gas regardless of temperature
- At high temperatures ( $T_R > 2$ ), ideal gas behavior can be assumed.
- The deviation is highest in the vicinity of the critical point.

### Example: Ideal Gas

Determine the specific volume of R-134a at 1 MPa and 50°C, using (a) ideal gas equation (b) the generalized compressibility chart. Compare the values obtained with the actual value of  $0.02171 \text{ m}^3/\text{kg}$ .

### Solution:

From Table A-1, for R-134a,  $R = 0.0815 \text{ kPa}\cdot\text{m}^3/(\text{kg}\cdot\text{K})$ ,  $P_{cr} = 4.067 \text{ MPa}$ , and  $T_{cr} = 374.3 \text{ K}$

(a) Ideal gas equation of state

$$v = \frac{RT}{P} = \frac{[0.0815 \text{ kPa}\cdot\text{m}^3/(\text{kg}\cdot\text{K})](323 \text{ K})}{(1000 \text{ kPa})} = 0.02632 \text{ m}^3/\text{kg}$$

Comparing with the tabulated value, using ideal gas equation one would get an error of  $(0.02632 - 0.02171)/0.02171 = 0.212$  or 21.2%.

(b) To determine the correction factor  $Z$ ,

$$P_R = \frac{P}{P_{cr}} = \frac{1 \text{ MPa}}{4.067 \text{ MPa}} = 0.246$$
$$T_R = \frac{T}{T_{cr}} = \frac{323 \text{ K}}{374.3 \text{ K}} = 0.863$$

From Fig. A-15,  $Z = 0.84$ . Thus,

$$v = Z v_{ideal} = 0.84 (0.02632 \text{ m}^3/\text{kg}) = 0.02211 \text{ m}^3/\text{kg}$$

The error is less than 2%.

Therefore, in the absence of exact tabulated data, the generalized compressibility chart can be used.

### Other Equations of States

Van der Waals Equation of State:

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

where.

$$a = \frac{27R^2T_{cr}^2}{64P_{cr}} \quad \text{and} \quad b = \frac{RT_{cr}}{8P_{cr}}$$

In this relationship, the intermolecular attraction forces and the volume occupied by molecules are considered.

Note: the accuracy of the Van der Waals equation of state is often inadequate.

Beattie-Bridgeman Equation of State

It is based on five experimentally determined constants:

$$P = \frac{R_u T}{\bar{v}^2} \left(1 - \frac{c}{\bar{v} T^3}\right) (\bar{v} + B) - \frac{A}{\bar{v}^2}$$

where

$$A = A_0 \left(1 - \frac{a}{\bar{v}}\right) \quad \text{and} \quad B = B_0 \left(1 - \frac{b}{\bar{v}}\right)$$

Constants appearing in the above equation are given in Table 3-4, Cengel book.