

Lecture 13

Equations of State

The relationship among the state variables, temperature, pressure, and specific volume is called the equation of state. We now consider the equation of state for the vapor or gaseous phase of simple compressible substances. A functional relationship among the properties is known as an equation of state.

$$F(P, T, v) \equiv 0$$

Ideal Gas

Combination of Boyle's and Charles' laws for gases at low pressure result in the equation of state for the ideal gas as

$$P = R \left(\frac{T}{v} \right)$$

where R is the constant of proportionality and is called the **gas constant** and takes on a different value for each gas. If a gas obeys this relation, it is called an ideal gas. We often write this equation as

$$Pv = RT \quad \text{The ideal gas equation of state may be written several ways.}$$

$$Pv = RT \quad PV = \frac{m}{M} (MR) T$$

$$P \frac{V}{m} = RT \quad PV = NR_u T$$

$$PV = mRT \quad P \frac{V}{N} = R_u T$$

$$P\bar{v} = R_u T$$

P = absolute pressure in MPa, or kPa

\bar{v} = molar specific volume in m³/kmol

v = specific volume in m³/kg

T = absolute temperature in K

R_u = 8.314 kJ/(kmol·K)

The ideal gas equation of state can be derived from basic principles if one assumes

1. Intermolecular forces are small.
2. Volume occupied by the particles is small

The ideal gas equation of state is used when

- (1) the pressure is small compared to the critical pressure or
- (2) when the temperature is twice the critical temperature and the pressure is less than 10 times the critical pressure.

Equations of State for Real Gases: Real gases are those which deviate from the ideal behavior.

Compressibility Factor

To determine how much the ideal gas equation of state deviates from the actual gas behavior,

we introduce the compressibility factor Z as follows.

$$Z = \frac{pv}{RT}$$

$$Z = \frac{v}{RT/p}$$

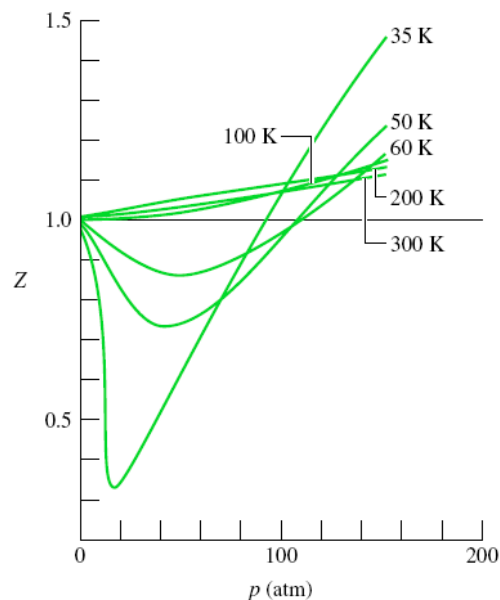
$\frac{RT}{p} = v_{ideal}$ that is the volume obtained from ideal gas equation of state

Therefore $z = \frac{v_{actual}}{v_{ideal}}$

Z represent to what factor a real gas is compressed (reduction in volume) in comparison with the ideal gas volume at a particular pressure

For an ideal gas $Z = 1$,

and the deviation of Z from unity measures the deviation of the actual P - V - T relation from the ideal gas equation of state.



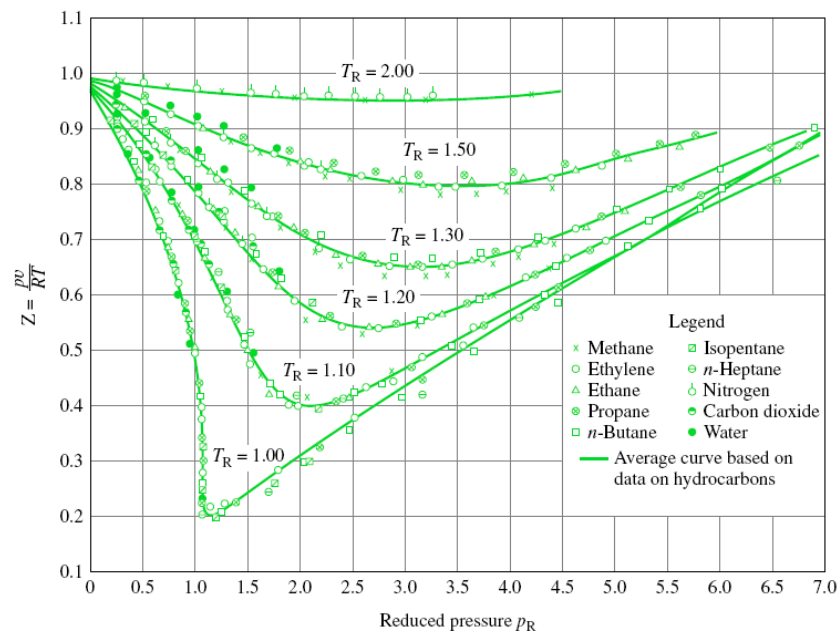
Variation of the compressibility factor of hydrogen with pressure at constant temperature.

- Similar charts have been prepared for other gases.
- they are found to be *qualitatively* similar
- when the coordinates are suitably modified, the curves for several different gases coincide closely when plotted together on the same coordinate axes
- The compressibility factor is expressed as a function of the reduced pressure and the reduced temperature.
- The Z factor is approximately the same for all gases at the same *reduced temperature* and *reduced pressure*

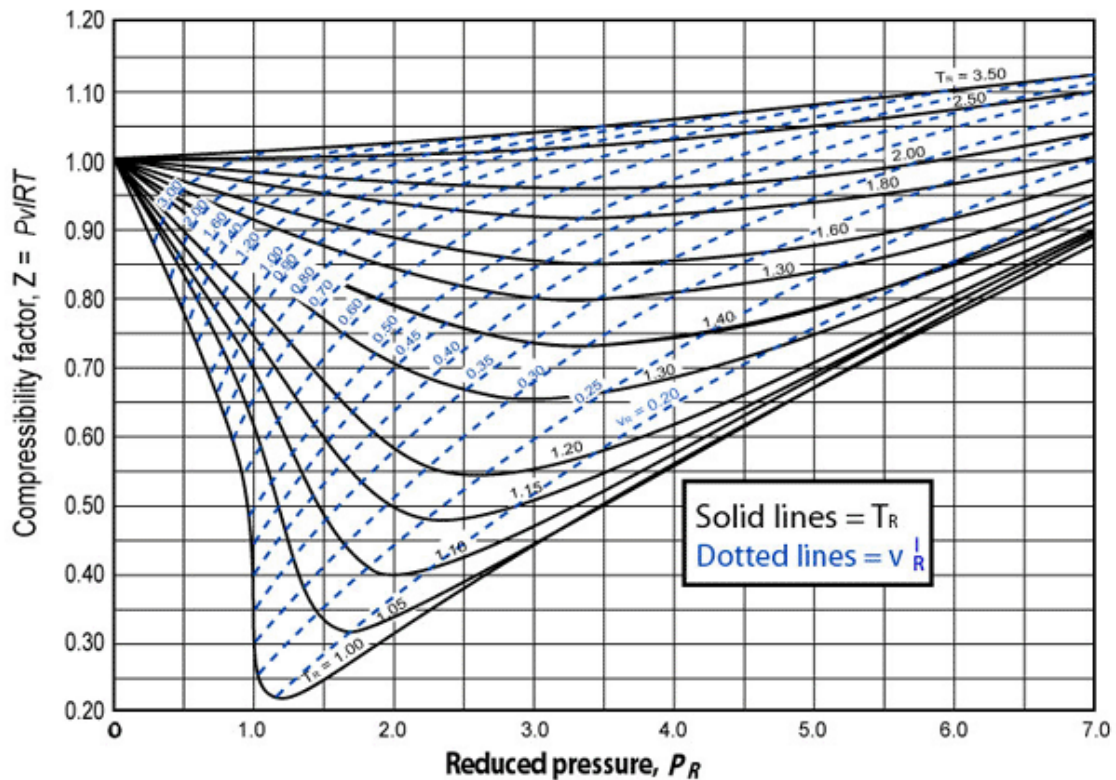
$$T_R = \frac{T}{T_{cr}} \quad \text{and} \quad P_R = \frac{P}{P_{cr}}$$

- This is referred to as the *principle of corresponding states*.

- Two gases are said to be in corresponding states when they have the same reduced pressure and reduced temperature



Generalised Compressibility Chart



Instead of reduced temperature pseudo reduced volume may be used.

Pseudo reduced volume $V_R = \frac{v_{actual}}{RT_{cr}/P_{cr}}$

Why Z factor is less than 1 at certain pressures and greater than 1 at higher pressures?

At certain high pressures Z value = 1. Can this be considered as an ideal gas at high pressures since Z=1?

$$Z = \frac{v_{actual}}{v_{ideal}}$$

If the Z value is less than 1 the actual volume is less than the ideal gas volume. i.e. the reduction in volume is more.

For Z value greater than 1 the actual volume is greater than the ideal gas volume, i.e. is compression is less.

This is because of the fact that in an ideal gas intermolecular forces are neglected. In a real gas intermolecular forces, **gravitational attraction** and **coulombic repulsion**, are considered.

At very low pressures gas molecules are far apart, therefore intermolecular forces are so small or negligible. That is when we consider a gas as ideal gas. So around $P = 0$, $Z = 1$.

When the pressure increases behaviour of the gas deviates from the ideal behaviour. At increased pressures the molecules come closer so gravitational attraction is more which brings the molecules closer than that of the ideal gas, i.e. the reduction in volume is more as compared to the ideal gas behaviour. That is why the Z value decreases initially (less than 1) to the lowest value of Z when pressure increases.

When the pressure is further increased molecules again comes closer, then the coulombic repulsion comes into picture. Now gas cannot be compressed to the extent as before (molecules does not come closer easily because of coulombic repulsion). The Z value now increases from the lowest value as the pressure increases and eventually reaches 1. Here this is not an ideal gas even though the Z value equals 1 because forces of interaction between the molecules are there, i.e. gravitational attraction and coulombic repulsion are balanced.

Now at higher pressures the molecules are very close so that the coulombic repulsion dominates over gravitational attraction. Here the actual volume of the real gas is greater than the ideal gas volume because compression is less because of coulombic repulsion. Therefore Z value is greater than 1.

Virial Expansion

$$Z = 1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \frac{D(T)}{v^3} + \dots$$

- The word *virial* stems from the Latin word for force
- B, C, D, \dots are called *virial coefficients* and they depend on temperature
- Virial expansions can be derived by the methods of statistical mechanics
- B/v accounts for two-molecule interactions,
- C/v^2 accounts for three-molecule interactions

Two constant Equation of state

a) van der Waals equation

In the ideal gas equation of state, $p v = RT$

- not all of the volume of a container would be available to the gas molecules
- the force they exert on the container wall would be reduced because of the attractive forces that exist between molecules

$$p = \frac{\bar{R}T}{\bar{v} - b} - \frac{a}{\bar{v}^2}$$

$\frac{a}{\bar{v}^2}$ is the force of cohesion and b is co-volume

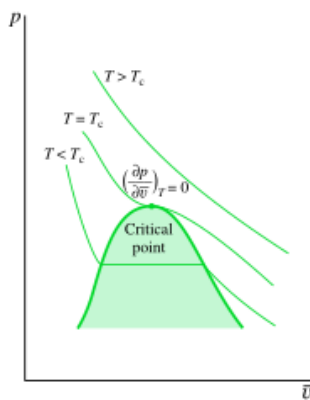
Here \bar{v} = molar specific volume in m³/kmol and \bar{R} = universal gas constant.

If specific volume, v is used then instead of \bar{R} use R i.e. the characteristic gas constant

To evaluate a and b

The critical isotherm passes through a point of inflection at the critical point, and the slope is zero there. These conditions are mathematically expressed as

$$\left(\frac{\partial^2 p}{\partial \bar{v}^2}\right)_T = 0, \quad \left(\frac{\partial p}{\partial \bar{v}}\right)_T = 0 \quad (\text{critical point})$$



the van der Waals equation at the critical point

$$p_c = \frac{\bar{R}T_c}{\bar{v}_c - b} - \frac{a}{\bar{v}_c^2}$$

Therefore

$$\begin{aligned} \left(\frac{\partial^2 p}{\partial \bar{v}^2}\right)_T &= \frac{2\bar{R}T_c}{(\bar{v}_c - b)^3} - \frac{6a}{\bar{v}_c^4} = 0 \\ \left(\frac{\partial p}{\partial \bar{v}}\right)_T &= -\frac{\bar{R}T_c}{(\bar{v}_c - b)^2} + \frac{2a}{\bar{v}_c^3} = 0 \end{aligned}$$

Solving the above equations for a , b and v_c we get

$$\begin{aligned} a &= \frac{27}{64} \frac{\bar{R}^2 T_c^2}{p_c} \\ b &= \frac{\bar{R}T_c}{8p_c} \\ \bar{v}_c &= \frac{3}{8} \frac{\bar{R}T_c}{p_c} \end{aligned}$$

Instead of \bar{R} use R i.e. the characteristic gas constant if the quantities are per unit mass.

b) Redlich–Kwong equation

$$p = \frac{RT}{v - b} - \frac{a}{v(v + b)\sqrt{T}}$$

c) Berthelot equation

$$p = \frac{RT}{v-b} - \frac{a}{Tv^2}$$

d) Dieterici equation

$$p = \frac{RT}{v-b} e^{\left(\frac{-a}{RTv}\right)}$$