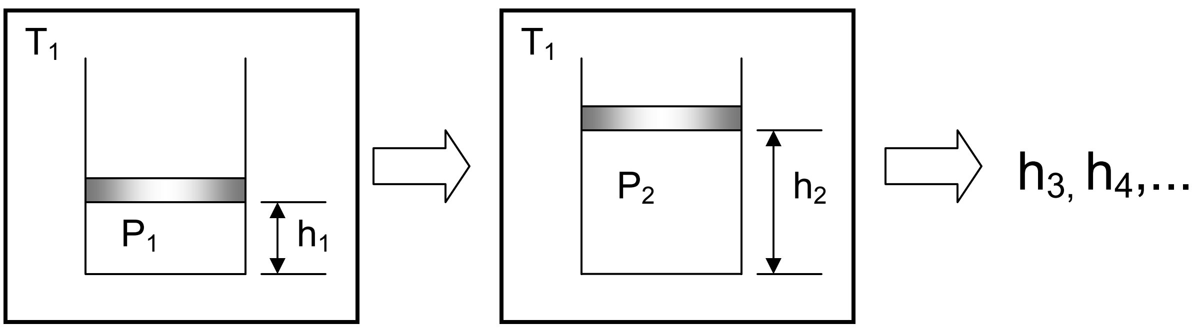
P-v-T Relations for Vapors (Gases)

Consider a fixed amount (# of moles) of gas in a piston-cylinder assembly held at constant temperature, say T_1.

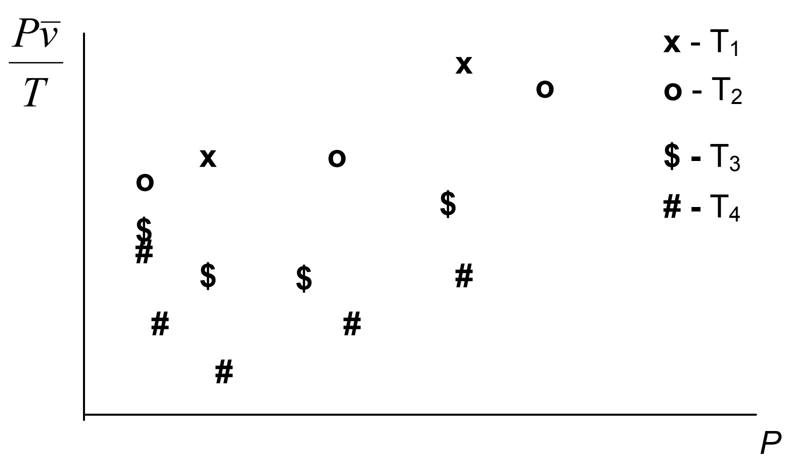
Move piston slowly to various positions, measure system pressure P and volume (via height h) at each equilibrium position



Repeat tests at different temperatures T_2, T_3,…

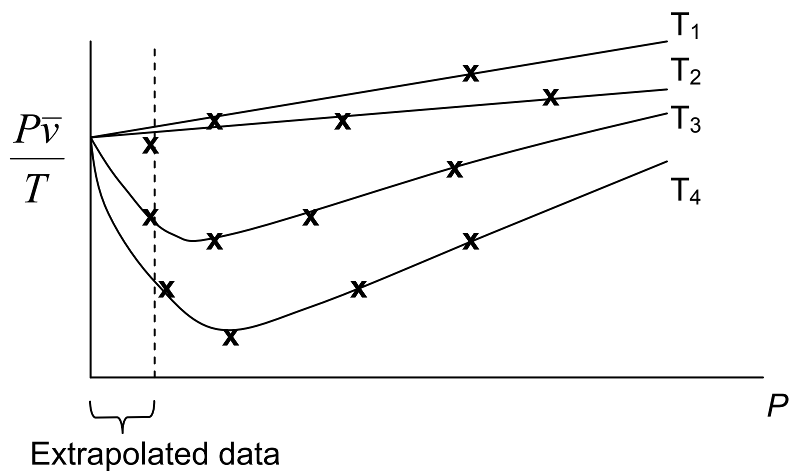
Define **molar specific volume** $\bar{v}$ as $\dfrac{volume}{\#moles}$ $\left(\dfrac{\mathrm{m}^3}{\mathrm{mol}}\right)$

Plot results as $\dfrac{P\bar{v}}{T}$ vs P



Since $P\bar{v}$ is a finite number, as $P \to 0$, $\bar{v} \to \infty$

As $\bar{v}$ (volume/#moles) approaches infinity continuum assumption fails have to extrapolate experimental data to P= 0



It is found that when the data is extrapolated to P= 0 you get a limiting value for $P\bar{v}/T$:

$$\lim_{P\to 0}\left(\frac{P\bar{v}}{T}\right) = \bar{R} \qquad \text{units}: \frac{\frac{\text{N}}{\text{m}^2}\left(\frac{m^3}{kmol}\right)}{{}^{\text{o}}K} = \frac{Nm}{kmol^oK}$$

The same value for $\bar{R}$ is found for all gases, hence it is referred to as the **Universal Gas Constant**

$$\bar{R} = 8314\,\frac{J}{kmol^oK} = 8.314\,\frac{kJ}{kmol^oK}$$

The ratio of the molar and mass specific volume defines the **Molar mass**, μ:

$$\frac{\bar{v}}{v} = \left(\frac{vol}{mol}\right)\frac{mass}{vol} = \frac{mass}{mol} = \mu$$

$$\bar{v} = \mu \cdot v$$

$$\lim_{P\to 0}\left(\frac{P\bar{v}}{T}\right) = \lim_{P\to 0}\left(\frac{P\mu v}{T}\right) = \bar{R}$$

$$\lim_{P\to 0}\left(\frac{Pv}{T}\right) = \frac{\bar{R}}{\mu}$$

Define the **gas constant** as, $\boxed{R = \bar{R}/\mu}$

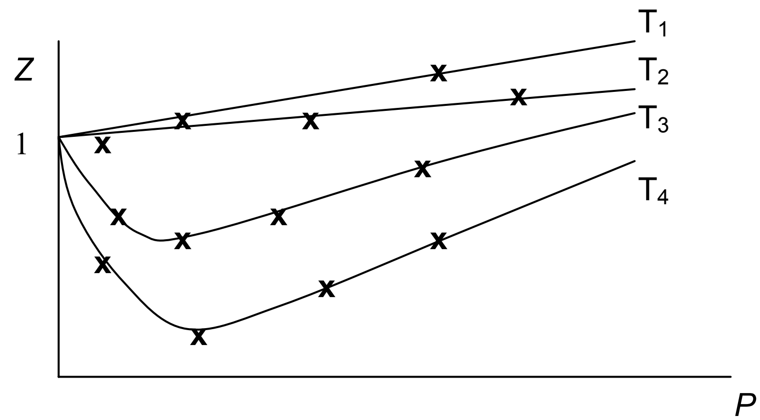
The gas constant for air is

$$R_{air} = \frac{\bar{R}}{\mu} = \left(8314\frac{J}{kmol^{o}K}\right)\left(\frac{kmol}{29kg}\right) = 286.7\frac{J}{kg^{o}K}$$

We define the **compressibility factor** Z as

$$Z = \frac{P\bar{v}}{\bar{R}T} = \frac{P(\mu v)}{(\mu R)T} = \frac{Pv}{RT}$$

Re-plotting data as Z vs P (as P→ 0, $\frac{P\bar{v}}{T} = \bar{R}$, Z→ 1)



Repeat experiments using different gases and get the same shape curves.

If we plot Z versus the **reduced pressure** P_R (=P/P_c) for different **reduced temperatures** T_R (=T/T_c) you get a universal set of curves known as the **generalized compressibility chart**

Molar mass and critical properties are given in Table A-1, for example:

T_c(air)= 133K T_c(water)= 647.3K
P_c(air)= 37.7 bar P_c(water)= 220.9 bar

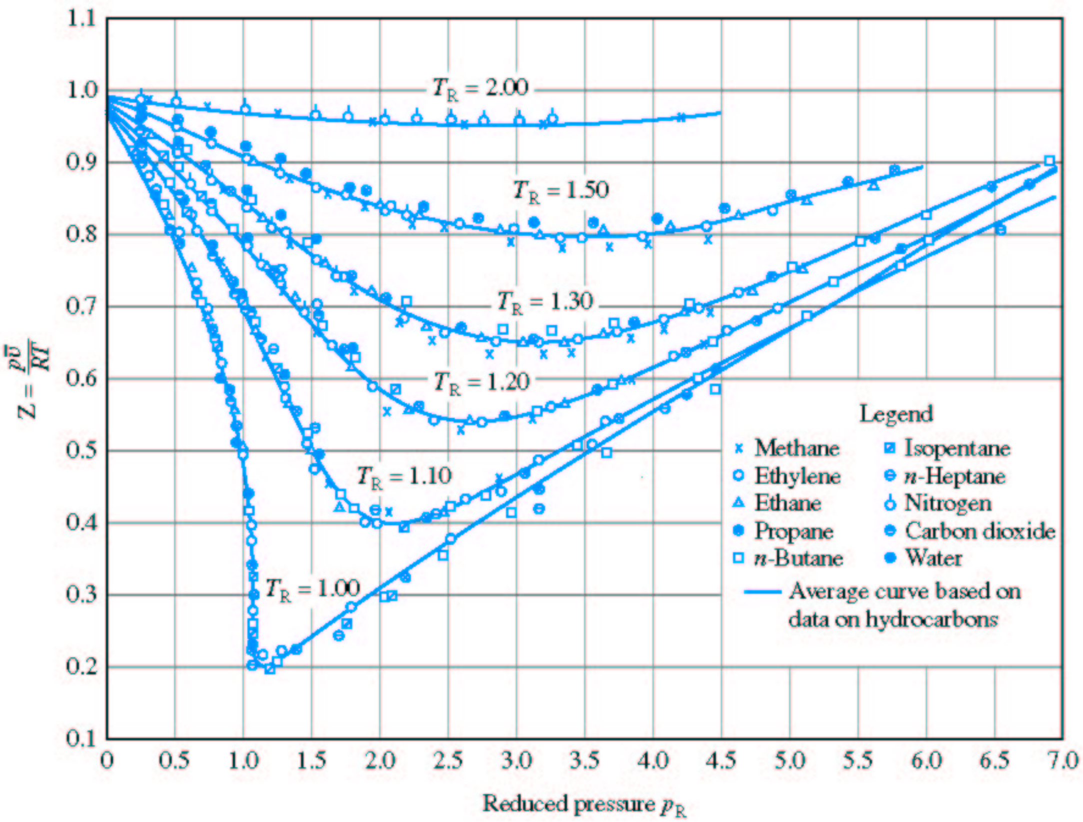


Figure 3.1.2

For a given gas with a gas constant R=$\bar{R}/\mu$, knowing the pressure and temperature you can use the above graph to get the specific volume $v = \dfrac{\bar{v}}{\mu}$

Z →1 (within 5%) for *low* reduced pressure ($P_R < 0.2$) independent of temperature, e.g. $P_{air} < 7.6$ bar

Z →1 (within 5%) for *high* reduced temperatures ($T_R > 2$) independent of pressure, e.g. for air $T_{air} > 266$K (-7C)

In most engineering applications we deal with gases at conditions that are within these limits, so $Z \rightarrow 1$

A gas for which Z can be assumed equal to one is called a **perfect gas**, or an **ideal gas**

For an ideal gas $Z = \frac{P\bar{v}}{\bar{R}T} = \frac{Pv}{RT} = 1$

$\boxed{P\bar{v} = \bar{R}T}$ and $\boxed{Pv = RT} \rightarrow \boxed{P = \rho RT}$

since $v = V/M$ and $\bar{v} = V/n$ n = # moles

so $\boxed{PV = n\bar{R}T}$ and $\boxed{PV = MRT}$

Microscopic Point of View

Molecules have KE associated with motion and PE associated with mutual attraction/repulsion. An ideal gas is one where the PE is negligible, e.g., billiard ball model.

At low pressure molecules are far apart so negligible PE
At high temp KE >> PE