Statistical Molecular Thermodynamics

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Video 2.5

Virial Equation of State

Virial Expansion

The compressibility is expressed as an infinite series expansion in either the density ($\overline{V}^{-1}$) or the pressure

$$Z = \frac{P\overline{V}}{RT} = 1 + \frac{B_{2V}(T)}{\overline{V}} + \frac{B_{3V}(T)}{\overline{V}^2} + \frac{B_{4V}(T)}{\overline{V}^3} + \ldots$$

$$Z = \frac{P\overline{V}}{RT} = 1 + B_{2P}(T)P + B_{3P}(T)P^2 + B_{4P}(T)P^3 + \ldots$$

B_{nX} are virial coefficients (B_{2V} is a “second” virial coefficient)

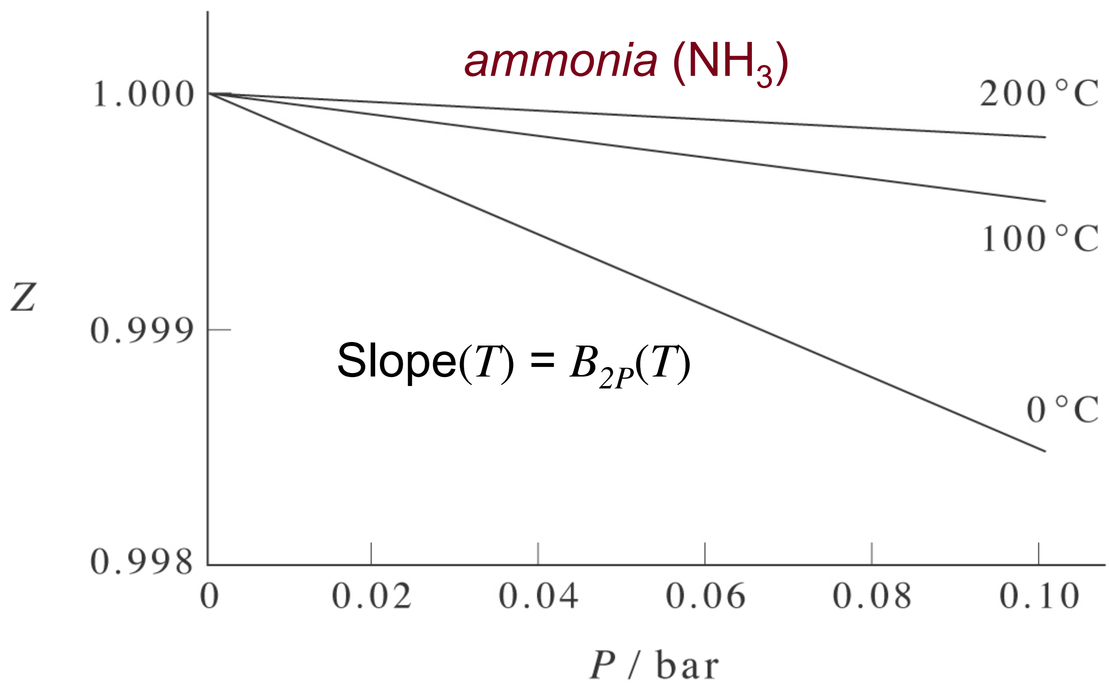
Note that at very low pressures or densities (large molar volumes) $Z \rightarrow 1$, reflecting ideal behavior.

THE 2ND VIRIAL COEFFICIENT

At low pressure

$$Z = 1 + B_{2P}(T)P$$

Z is linear in B_{2P} ➡



Through manipulation of the two virial expansions, one can also show that ➡ $B_{2V}(T) = RT\,B_{2P}(T)$

Virial Terms for Argon at 298 K

$$1 + \frac{B_{2V}(T)}{\overline{V}} + \frac{B_{3V}(T)}{\overline{V}^2} + (\cdots)$$

P (bar)	
1	1 - 0.00064 + 0.0000 + (0.00000)
10	1 - 0.00648 + 0.0020 – (0.00007)
100	1 - 0.06754 + 0.0213 – (0.00036)

units of B_{2V}:

volume•mol^{-1}

What Does B_{2V} "Mean"?

At low pressure: $$\frac{P\bar{V}}{RT} = 1 + B_{2P}(T)P$$

or: $$\bar{V} = \frac{RT}{P} + RTB_{2P}(T)$$

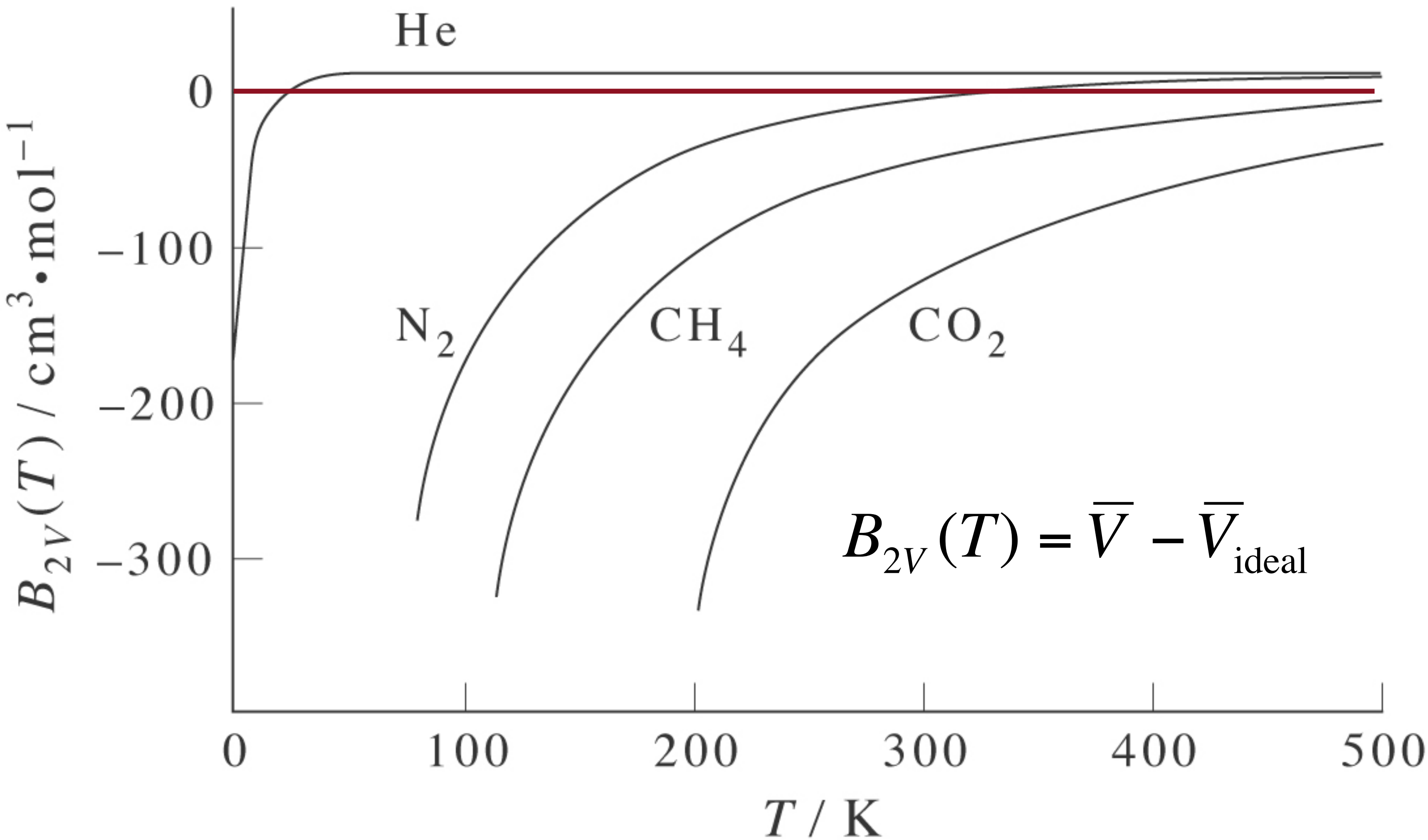
$\frac{RT}{P}$ ← $\bar{V}_{\text{ideal}}$ $RTB_{2P}(T)$ ← $B_{2V}(T)$

so: $$\bar{V} = \bar{V}_{\text{ideal}} + B_{2V}(T)$$

or: $$B_{2V}(T) = \bar{V} - \bar{V}_{\text{ideal}}$$

B_{2V} is the *difference* between the observed molar volume and the ideal gas molar volume

$B_{2V}(T)$ for Various Gases



$$B_{2V}(T) = \overline{V} - \overline{V}_{\text{ideal}}$$

Again: attractive forces dominate at low T, repulsive at high T