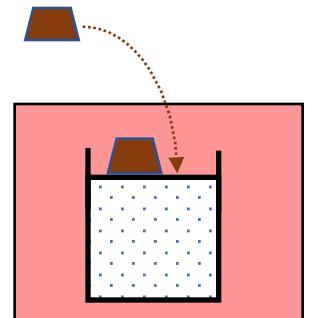
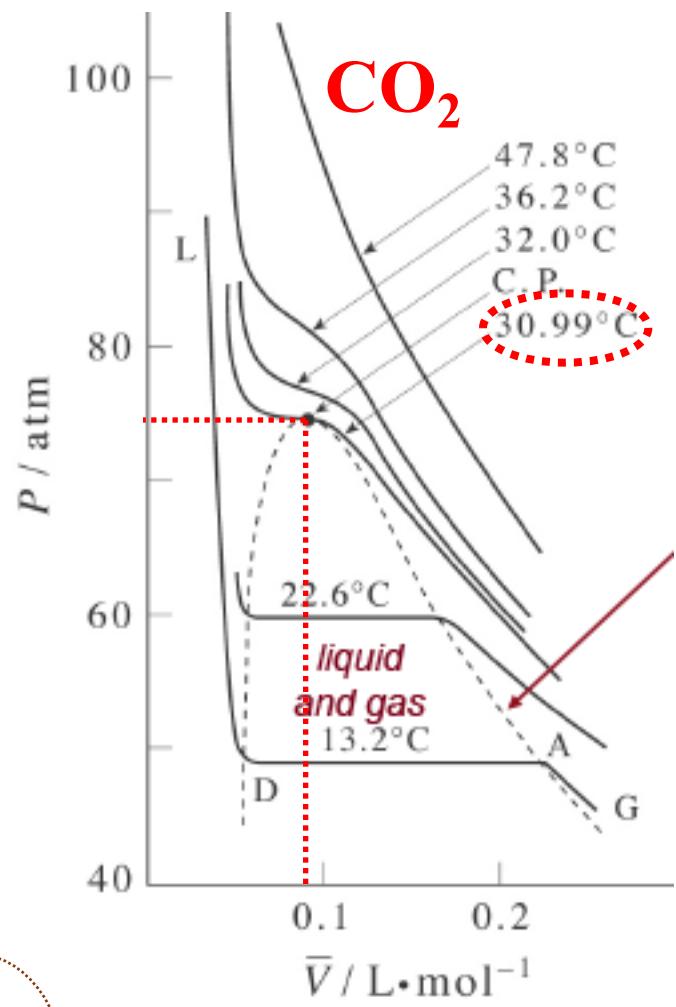


## **Law of Corresponding States (continue)**

Source of Slides : Internet.

Prof. Cris Cramer, University of Minnesota



Hot-Plate ( $T = 13.2^\circ\text{C}$ )

## CRITICAL COMPRESSIBILITY

TABLE 2.5

The experimental critical constants of various substances.

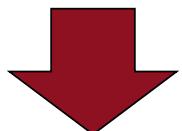
Species	$T_c/\text{K}$	$P_c/\text{bar}$	$P_c/\text{atm}$	$\bar{V}_c/\text{L}\cdot\text{mol}^{-1}$	$P_c\bar{V}_c/RT_c$
Helium	5.1950	2.2750	2.2452	0.05780	0.30443
Neon	44.415	26.555	26.208	0.04170	0.29986
Argon	150.95	49.288	48.643	0.07530	0.29571
Krypton	210.55	56.618	55.878	0.09220	0.29819
Hydrogen	32.938	12.838	12.670	0.06500	0.30470
Carbon dioxide	304.14	73.843	72.877	0.09400	0.27443

$$\frac{P_c\bar{V}_c}{RT_c} = \frac{1}{R} \left( \frac{a}{27b^2} \right) (3b) \left( \frac{27bR}{8a} \right) = 0.375!$$

*there is an apparent correspondence between different “real” gases that is entirely independent of the van der Waals equation of state*

## A REDUCED EQUATION OF STATE

$$\left(P + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT \quad \bar{V}_c = 3b \quad P_c = \frac{a}{27b^2} \quad T_c = \frac{8a}{27bR}$$

 Home WORK

$$\left(P_R + \frac{3}{\bar{V}_R^2}\right)\left(\bar{V}_R - \frac{1}{3}\right) = \frac{8}{3}T_R \quad P_R = \frac{P}{P_c} \quad \bar{V}_R = \frac{\bar{V}}{\bar{V}_c} \quad T_R = \frac{T}{T_c}$$

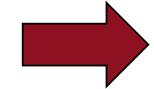
universal equation for *all* gases

reduced quantities

This is an example of the Law of Corresponding States:  
all gases have the same properties if compared at  
corresponding conditions.

# UNIVERSAL COMPRESSIBILITY FACTOR

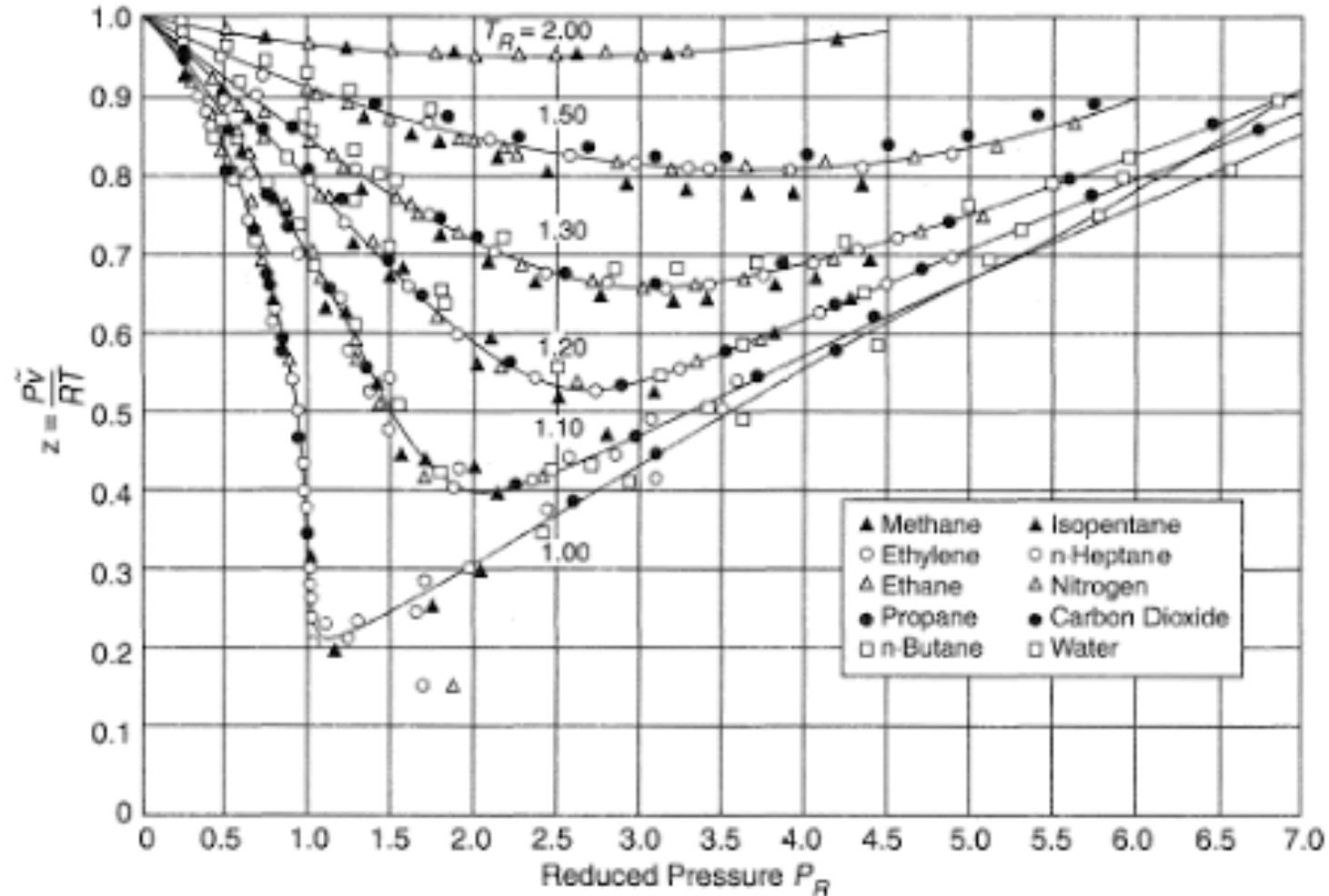
$$Z = \frac{P\bar{V}}{RT}$$



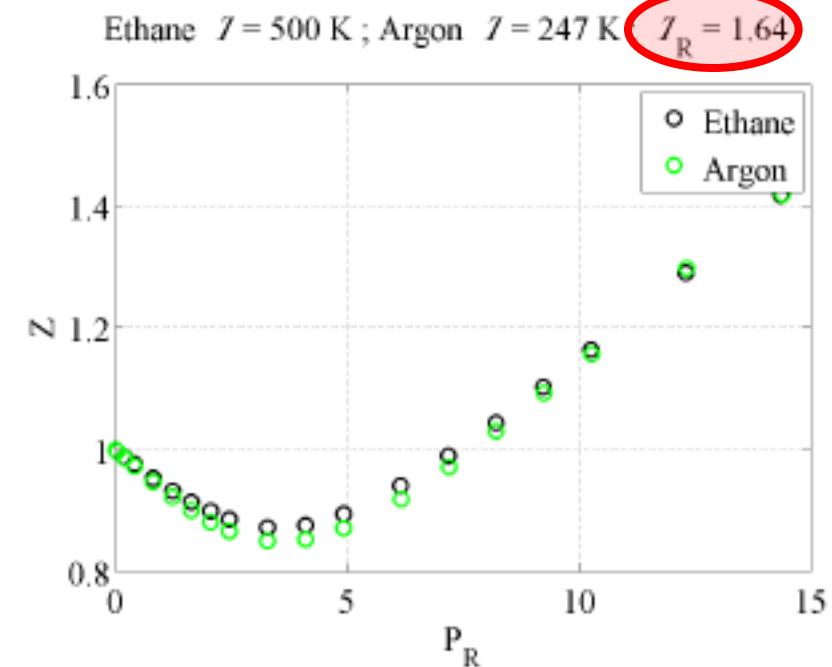
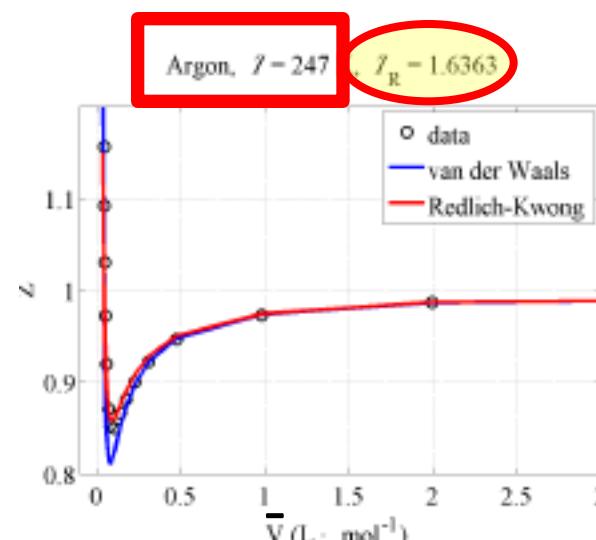
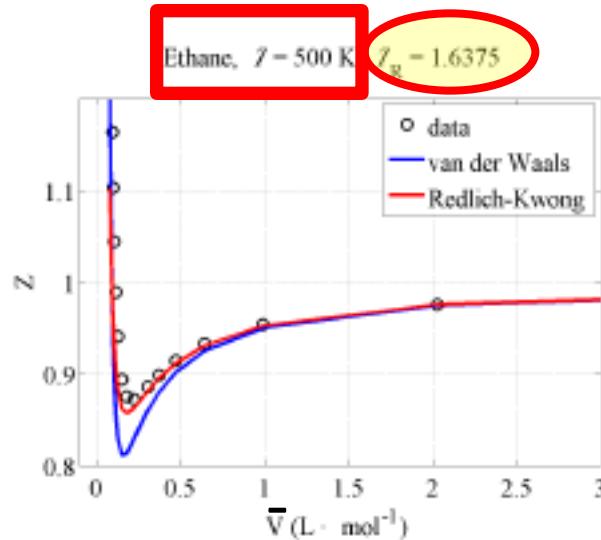
$$= \frac{3\bar{V}_R}{3\bar{V}_R - 1} - \frac{9}{8\bar{V}_R T_R}$$

for vdW equation of state

Again, at “corresponding conditions” (relative to critical data), all gases behave equivalently.



## LAW OF CORRESPONDING STATES EXAMPLE



## Home Work: Derive the following

$$Z = \frac{P\bar{V}}{RT}$$



$$= \frac{3\bar{V}_R}{3\bar{V}_R - 1} - \frac{9}{8\bar{V}_R T_R}$$

*for vdW equation of state*

# **Virial Equation of state**

## VIRIAL EXPANSION

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

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

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

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

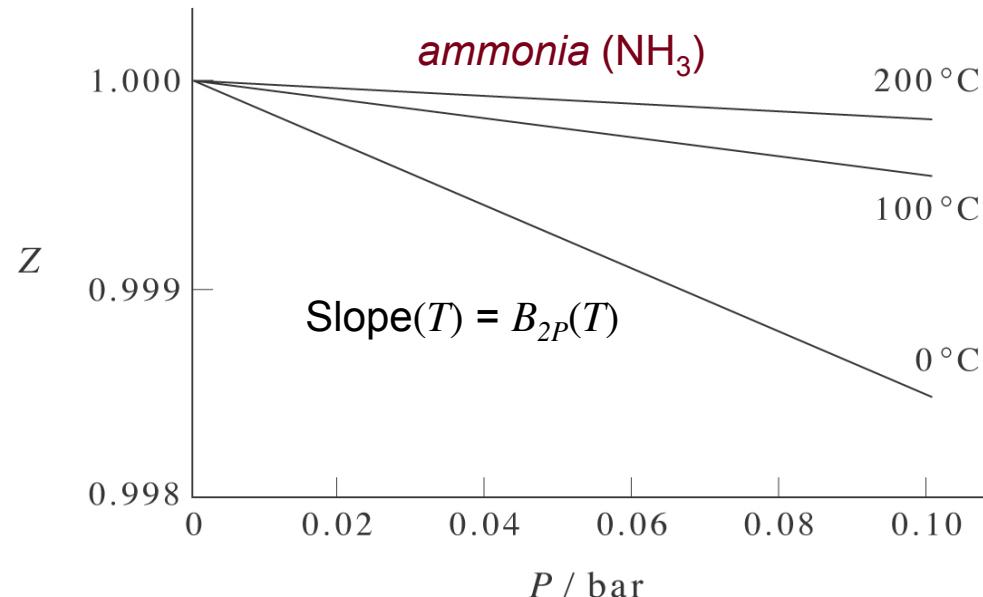
Note that at very low pressures or densities (large molar volumes)  $Z \rightarrow 1$ , reflecting ideal behavior.

## THE 2<sup>ND</sup> VIRIAL COEFFICIENT

At low pressure

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

$Z$  is linear in  $B_{2P}$   $\rightarrow$



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

## VIRIAL TERMS FOR ARGON AT 298 K

$$1 + \frac{B_{2V}(T)}{\bar{V}} + \frac{B_{3V}(T)}{\bar{V}^2} + (\dots)$$

$P$  (bar) —————

units of  $B_{2V}$ :

volume $\cdot$ mol $^{-1}$

$$1 \quad 1 - 0.00064 + 0.0000 + (0.00000)$$

$$10 \quad 1 - 0.00648 + 0.0020 - (0.00007)$$

$$100 \quad 1 - 0.06754 + 0.0213 - (0.00036)$$

## WHAT DOES $B_{2V}$ “MEAN”?

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

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

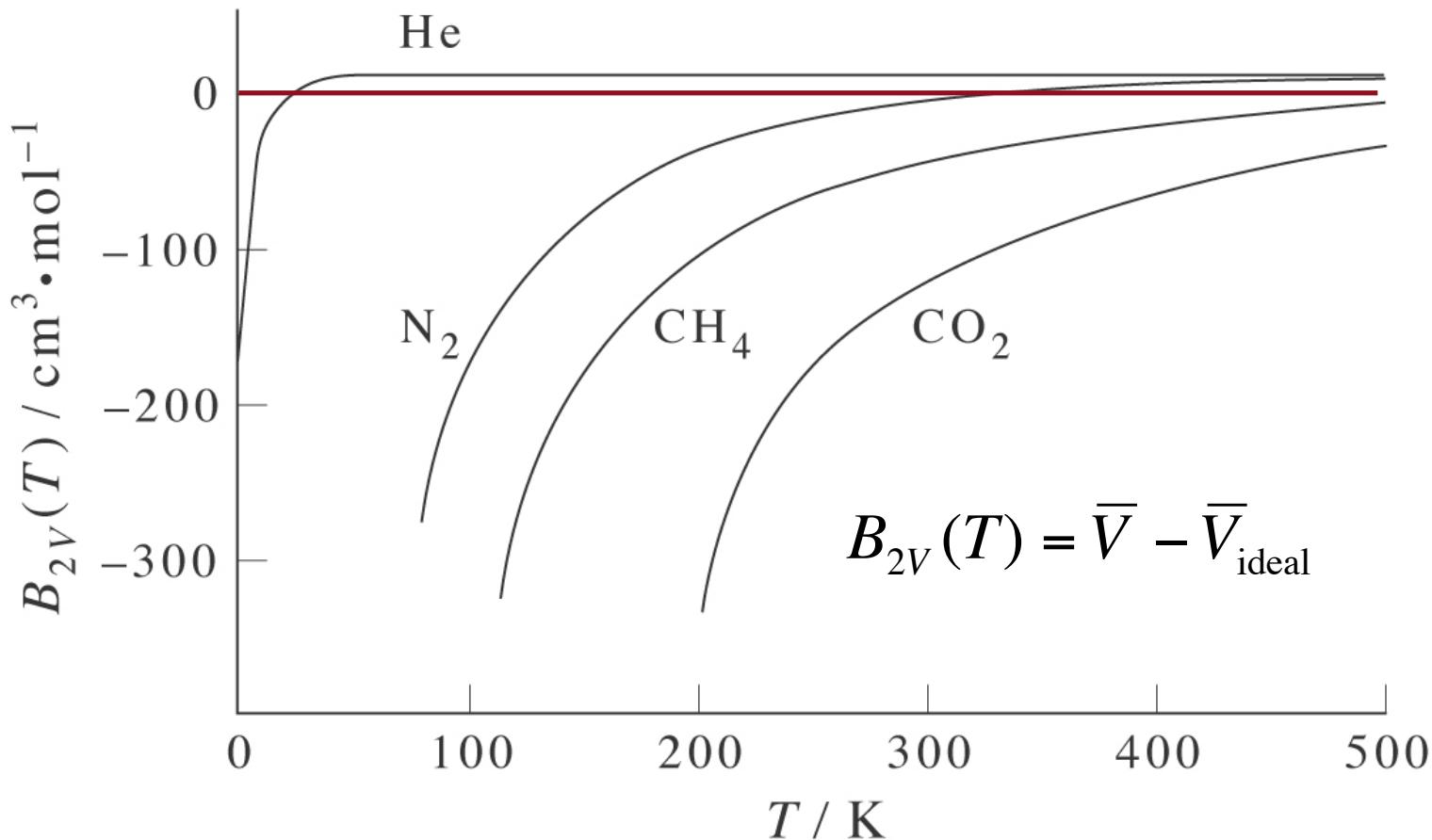
$\overline{V}_{\text{ideal}}$                                    $B_{2V}(T)$

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

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

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

## $B_{2V}(T)$ FOR VARIOUS GASES



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

# Van der Waals gas => 2<sup>nd</sup> Virial coefficient => “Boyle Temperature”

$$\frac{V_{DW}}{(P + \frac{a}{V^2})(V - b)} = RT$$

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

$$\Rightarrow P = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$\Rightarrow \frac{P}{RT} = \frac{1}{V - b} - \frac{a}{RTV^2}$$

$$\Rightarrow \frac{PV}{RT} = \frac{V}{V - b} - \frac{a}{RTV}$$

$$\Rightarrow Z = \frac{V}{V - b} - \frac{a}{RTV}$$

$$Z = \frac{1}{\left(1 - \frac{b}{V}\right)} - \frac{a}{RTV}$$

↑ Compressibility  
↓ repulsion  
attraction

Taylor Series

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \dots \quad [\text{if } |x| < 1]$$

$$\therefore Z = \left[ 1 + \frac{b}{V} + \underbrace{\left(\frac{b}{V}\right)^2 + \left(\frac{b}{V}\right)^3 + \dots}_{\text{negligible}} \right] - \frac{a}{RTV}$$

$$\Rightarrow Z = 1 + \frac{b}{V} - \frac{a}{RTV} \quad \text{--- ①}$$

$$\Rightarrow Z = 1 + \frac{1}{V} \left( b - \frac{a}{RT} \right)$$

Now, we know virial expansion

$$Z = 1 + \frac{B_{2V}(T)}{V} + \frac{B_{3V}(T)}{V^2} + \dots \quad \text{--- ②}$$

Comparing eqn. ① & ②

$$B_{2V}(T) = b - \frac{a}{RT}$$

Case 1 High Temp:  $\Rightarrow B_{2V}(T) = b - 0$

$$\therefore Z = \left(1 + \frac{b}{V}\right) \quad [Z > 1]$$

Case 2 very low Temp:  $\Rightarrow B_{2V}(T) = -\frac{a}{RT}$

$$Z < 1$$

Case III

$$At T = T_b, b = \frac{a}{RT_b} \Rightarrow B_{2V}(T) = 0$$

$$\therefore Z = 1 \quad \text{at } T = T_b$$

Boyle Temperature

Attraction & repulsion  
cancel each other  $\Rightarrow$  IDEAL  
BEHAVIOUR

# Review of L1-L3

- The ideal gas EOS  $PV=nRT$ 
  - The compressibility  $Z = PV/nRT$
  - Gases are rarely ideal (only at very low pressure)
  - van der Waals EOS can predict non-ideal gas behavior (also Saha-Basu, Redlich-Kwong and Peng-Robinson)
  - All “cubic EOS” are capable of describing the liquid and gaseous regions of  $PV$  isotherms
  - At the critical point, the vdW EOS has only one root, which permits estimation of vdW constants  $a$  and  $b$  experimentally
- The Law of Corresponding States says that all gases have the same properties if compared at “corresponding conditions”
  - “Corresponding conditions” means relative to their respective critical properties.
  - The virial expansion is an equation of state whose coefficients relate directly to intermolecular interactions
  - The second virial coefficient  $B_{2v}$  measures the deviation of the volume of a real gas compared to an ideal one under the same temperature and pressure.



# Next (L4):

## Tutorial based on L1-L3