Gen Chem Revisited

GAS-1

One of the most familiar relationships in chemistry is the *ideal gas equation of state*

$$PV = nRT$$

Sometimes written as:

$$P\overline{V} = RT \qquad \overline{V} = ??$$

Gases that obey this equation behave *ideally*.

The ideal gas equation of state neglects:

1. The molecular size of gases.
2. Intermolecular interactions of gases.

Under what conditions is this neglect legitimate?

Some Definitions

GAS-2

mass

Energy

Extensive Variable: Depends on the size of the system (e.g., V, m, E)

Intensive Variables: Doesn't depend on the size of the system (e.g., T, P, ρ)

Density

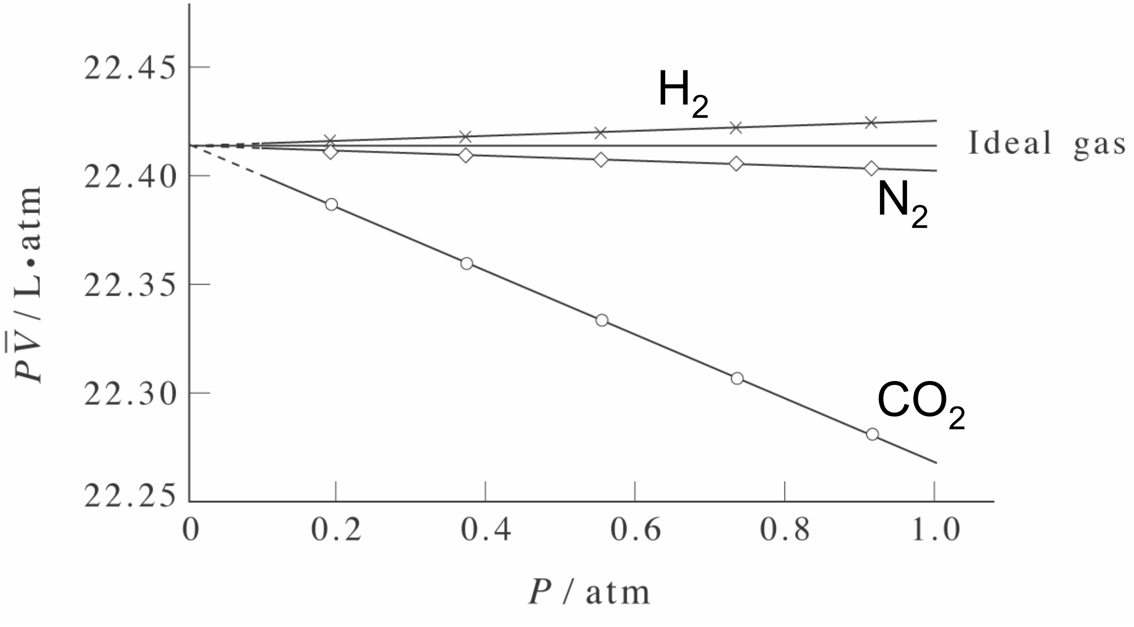
What about *molar volume*?

Operational Definition of Temperature (unit of kelvin, K):

$$T = \lim_{P \to 0} \frac{P\overline{V}}{R}$$

$$t/^{\circ}C = T/K - 273.15$$

Gases are Rarely Ideal! I



Measurements at 273.15 K (0 °C)

At low enough pressures, *all* gases behave ideally.

$$P\bar{V}(273.15) = 22.414 \text{ L·atm·mol}^{-1}$$

$$R = \frac{P\bar{V}}{T} = 0.082058 \text{ L·atm·mol}^{-1}\text{·K}^{-1} = 8.314 \text{ J·mol}^{-1}\text{·K}^{-1}$$

(see Table 16.2)

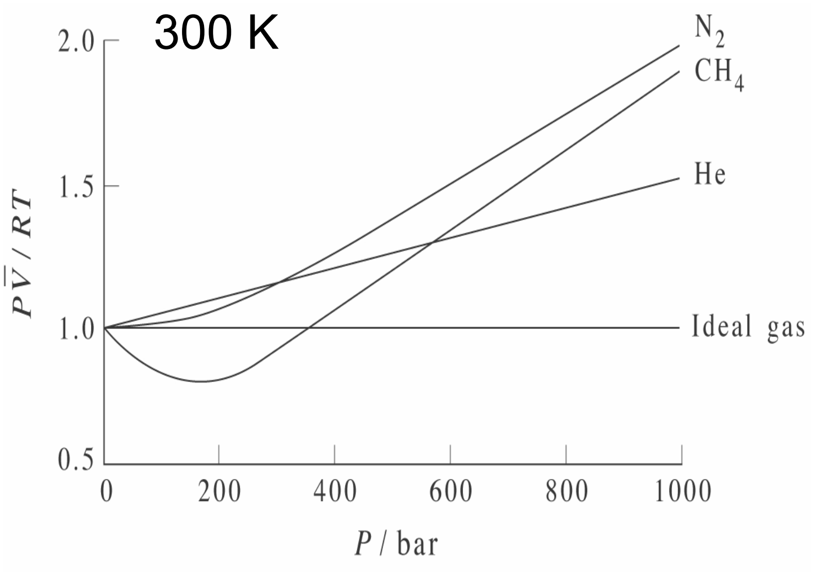
Gases are Rarely Ideal! II

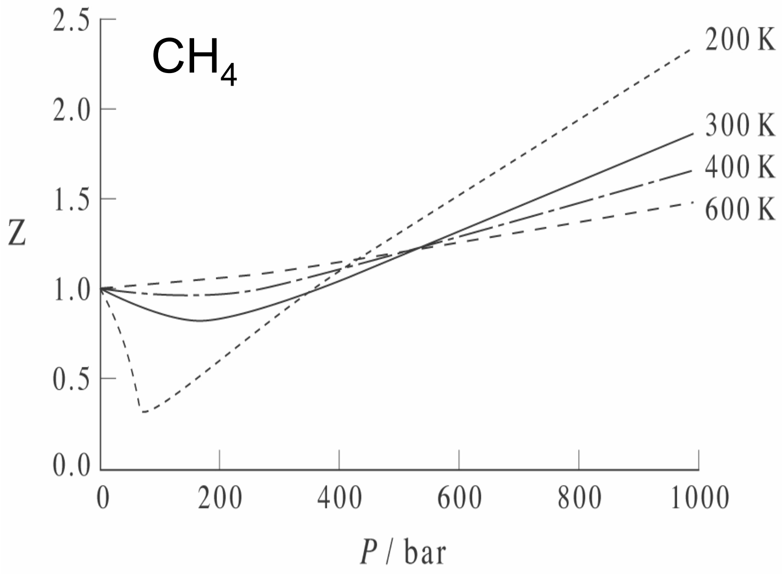
$$Z = \frac{P\overline{V}}{RT}$$

Compressibility

Units?

Ideal Gas?





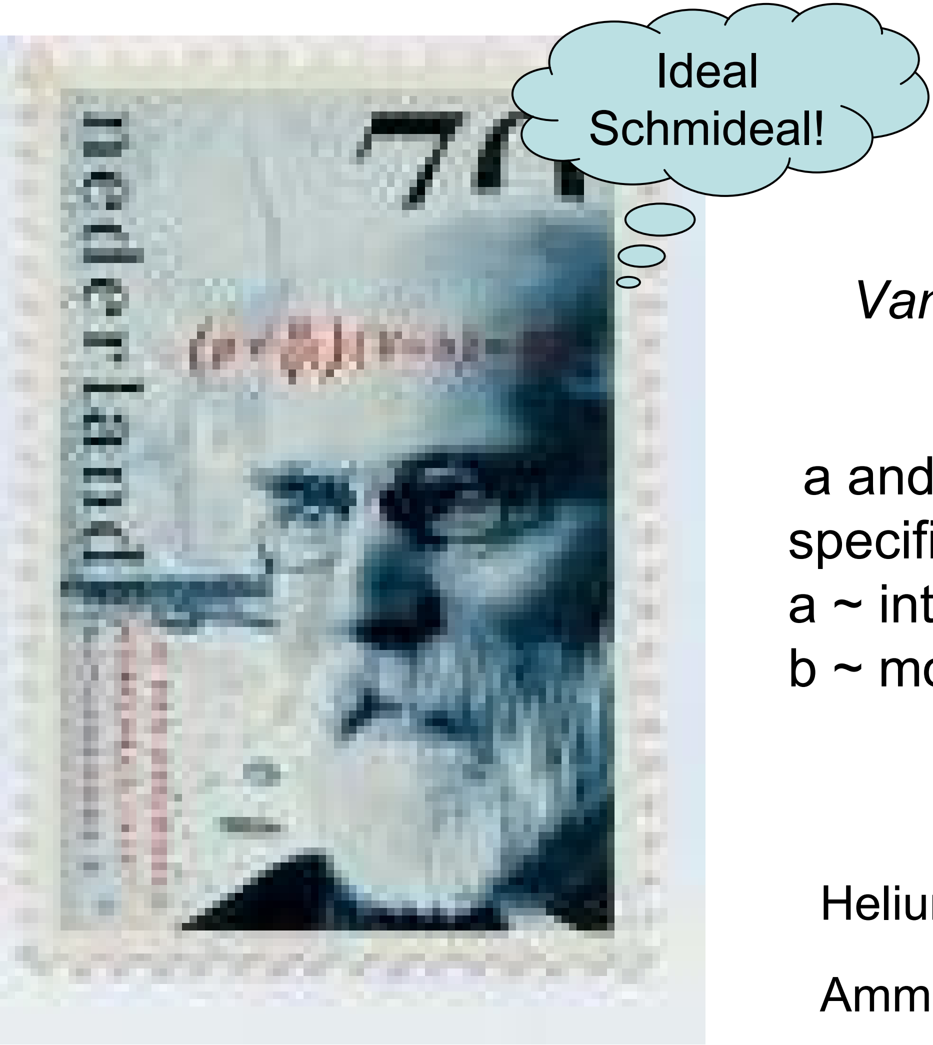
Low Temperature: Attractive forces

$$\overline{V}_{real} < \overline{V}_{ideal}$$

High Temperature: Repulsive forces

$$\overline{V}_{real} > \overline{V}_{ideal}$$

Johannes Diderik van der Waals



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

*Van der Waals Equation of State**

a and b are constants that depend on the specific gas in question:
a ~ intermolecular interaction strength
b ~ molecular size

	a ($dm^6 \cdot bar \cdot mol^{-2}$)	b ($dm^3 \cdot mol^{-1}$)
Helium	0.035	0.024
Ammonia	4.304	0.037

*This (and other equations of state) are cubic equations in terms of volume (this will become important!).

Other EOS

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

van der Waals

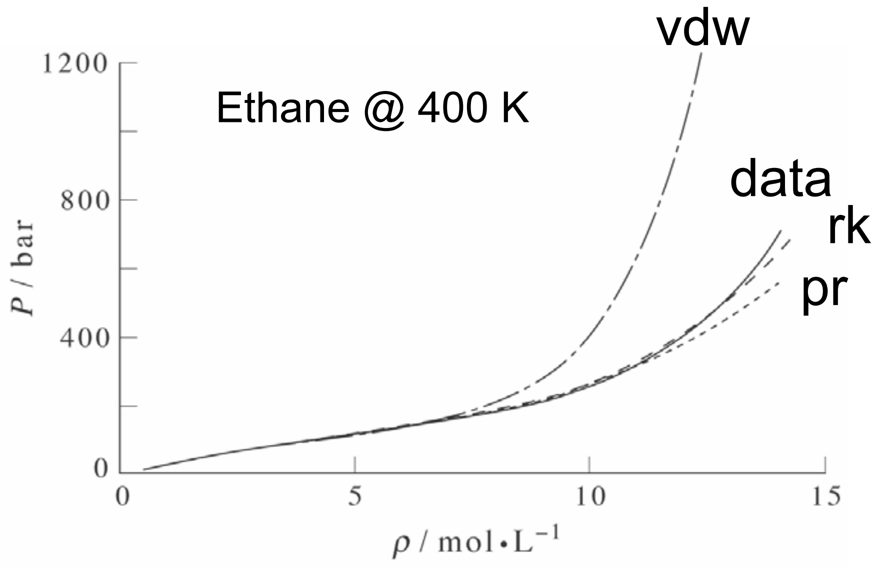
$$P=\frac{RT}{\overline{V}-B}-\frac{A}{T^{1/2}\overline{V}(\overline{V}+B)}$$

Redlich-Kwong

$$P=\frac{RT}{\overline{V}-\beta}-\frac{\alpha}{\overline{V}(\overline{V}+\beta)+\beta(\overline{V}-\beta)}$$

Peng-Robinson

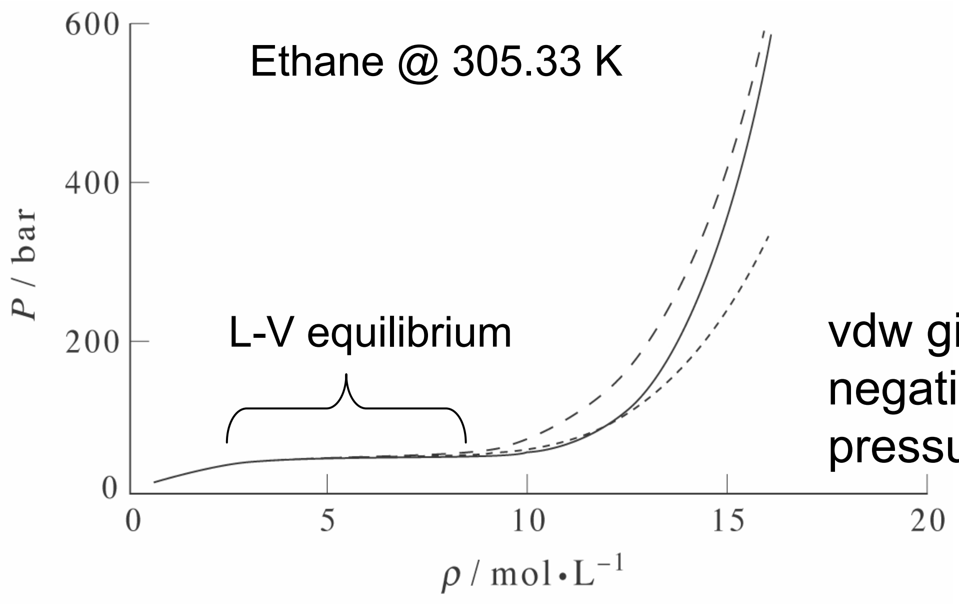
vdw, rk, pr EOS



$$\overline{V}^{-1} = \rho$$ Units?

What would ideal gas law predict for such a plot?

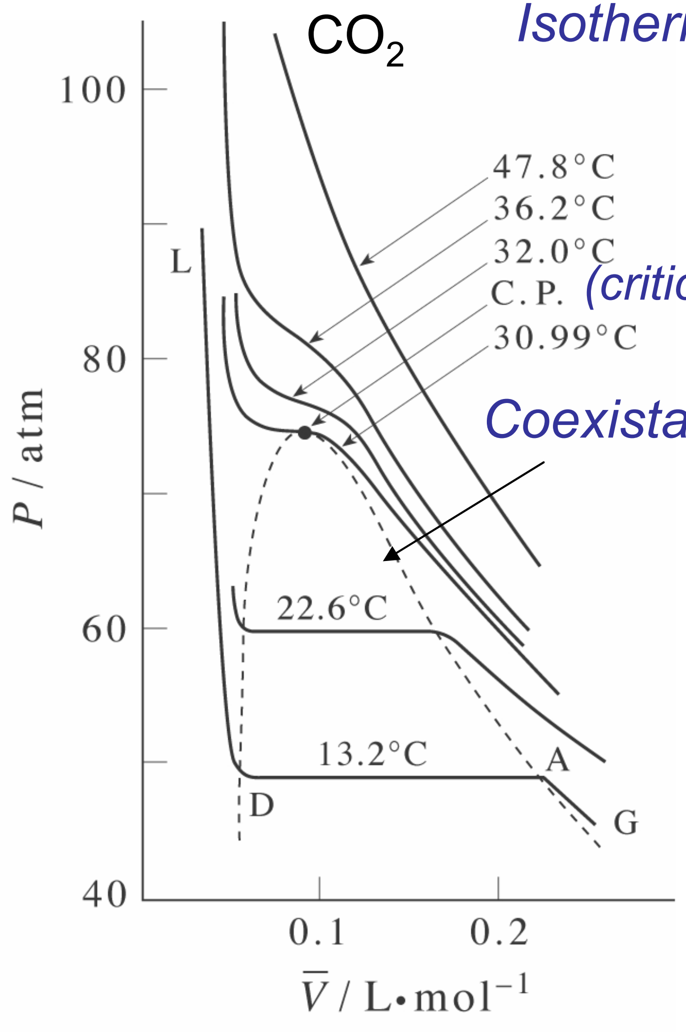
These EOS describe gas properties well – and are nearly quantitative when the gas liquefies!



vdw gives negative pressures!

Cubic Equations of State

Isotherms (plots of P vs V at constant T)



(critical pt)

Coexistance curve

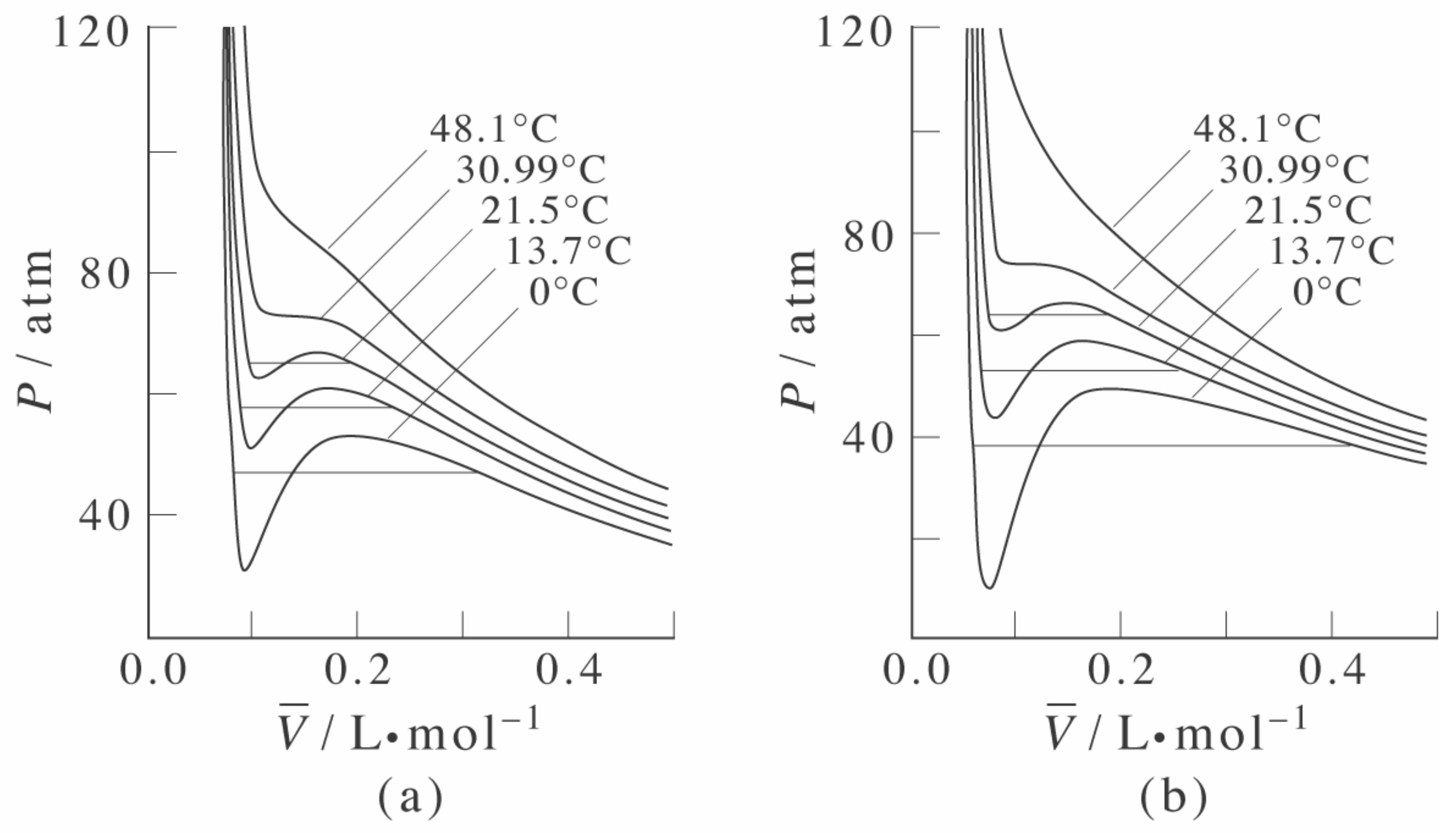
Cubic EOS describe both the liquid and gaseous regions

The temperature above which a gas can not be liquefied is called the critical temperature (T_c).

At T < T_c, there are horizontal regions (gas and liquid co-exist).

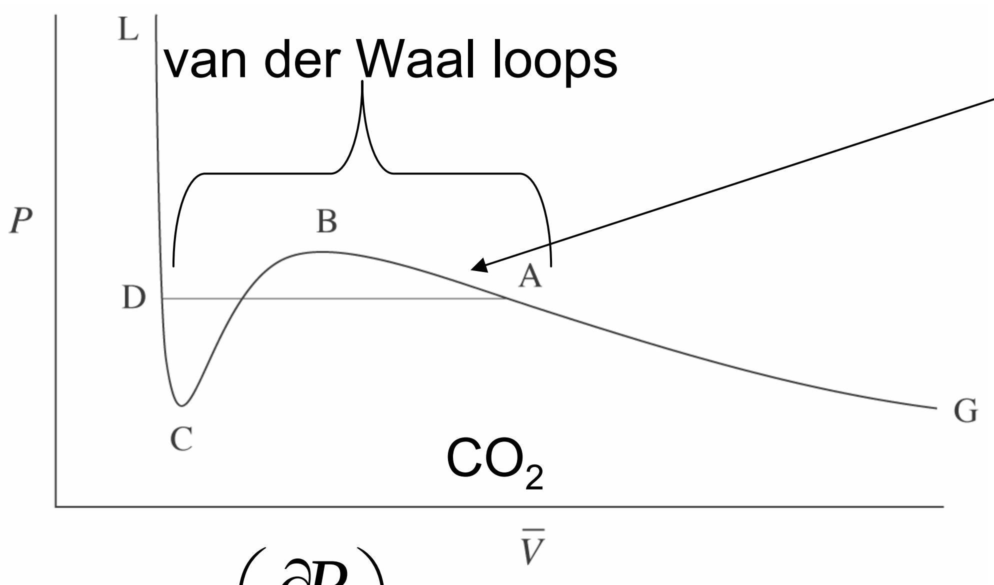
G to A to D to L (@ 13.2 °C)
a i
s q

How do cubic EOS do for CO_2?



Not too bad…

VDW P-V isotherm at T<T$_c$



Line DA is drawn such that areas of the loop both above and below DA are equal = Maxwell equal-area construction

What is sign of $\left(\frac{\partial P}{\partial \bar{V}}\right)_T$ from B to C? Is this realistic?

Three values of volume for a given pressure at T < T$_c$.

Remember: VDW EOS can be written as a cubic equation in molar volume!

$$\bar{V}^3 - \left(b + \frac{RT}{P}\right)\bar{V}^2 + \frac{a}{P}\bar{V} - \frac{ab}{P} = 0$$

Three roots!

Critical Point in VDW P-V Isotherms

$$\bar{V}^3 - \left(b + \frac{RT}{P}\right)\bar{V}^2 + \frac{a}{P}\bar{V} - \frac{ab}{P} = 0$$

At T > T_c only one real root.
At T < T_c three real roots.
At T=T_c all three roots merge.

At T = Tc …

$$\bar{V} - \bar{V}_c = 0$$

or

$$\left(\bar{V} - \bar{V}_c\right)^3 = 0$$

$$\bar{V}^3 - 3\bar{V}_c\bar{V}^2 + 3\bar{V}_c^{\,2}\bar{V} - \bar{V}_c^{\,3} = 0$$

Compare to VDW EOS and do some algebra…

$$\bar{V}_c = 3b \qquad P_c = \frac{a}{27b^2} \qquad T_c = \frac{8a}{27bR}$$

Critical Point in VDW P-V Isotherms

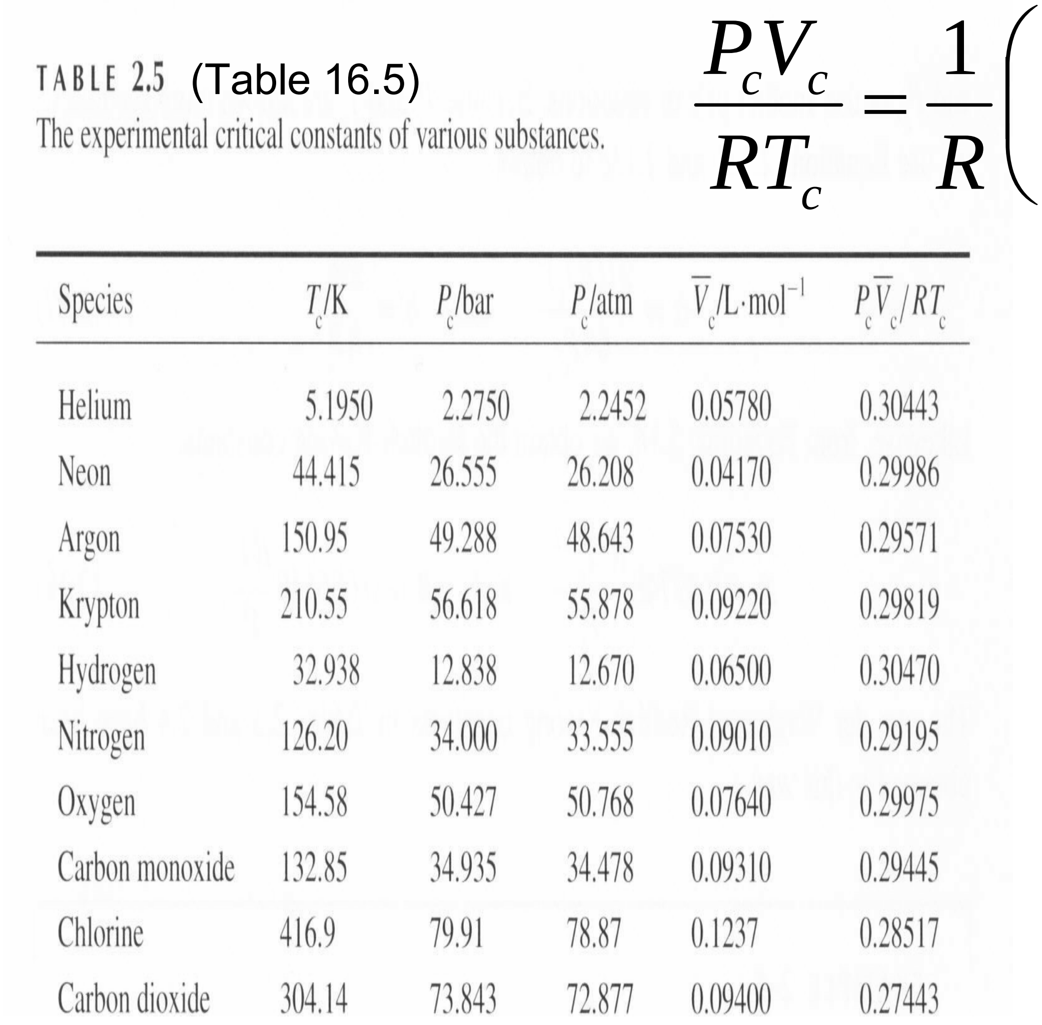


TABLE 2.5 (Table 16.5)

The experimental critical constants of various substances.

Species	T_c/K	P_c/bar	P_c/atm	$\overline{V}_c$/L·mol^{-1}	$P_c\overline{V}_c/RT_c$
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
Nitrogen	126.20	34.000	33.555	0.09010	0.29195
Oxygen	154.58	50.427	50.768	0.07640	0.29975
Carbon monoxide	132.85	34.935	34.478	0.09310	0.29445
Chlorine	416.9	79.91	78.87	0.1237	0.28517
Carbon dioxide	304.14	73.843	72.877	0.09400	0.27443

$$\frac{P_cV_c}{RT_c} = \frac{1}{R}\left(\frac{a}{27b^2}\right)(3b)\left(\frac{27bR}{8a}\right) = ??$$

$$\frac{P_c\overline{V}_c}{RT_c} =$$

An example of the *Law of Corresponding States*

Law of Corresponding States

In practice, the experimental values for the critical temperature and pressure are used to get *a* and *b.*

$$a = \frac{27(RT_c)^2}{64P_c} \qquad b = \frac{RT_c}{8P_c}$$

VDW equation with *a* and *b* substituted with above equations:

$$\left(P + \frac{3P_c\overline{V}_c^{\,2}}{\overline{V}^{\,2}}\right)\left(\overline{V} - \frac{1}{3}\overline{V}_c\right) = RT$$

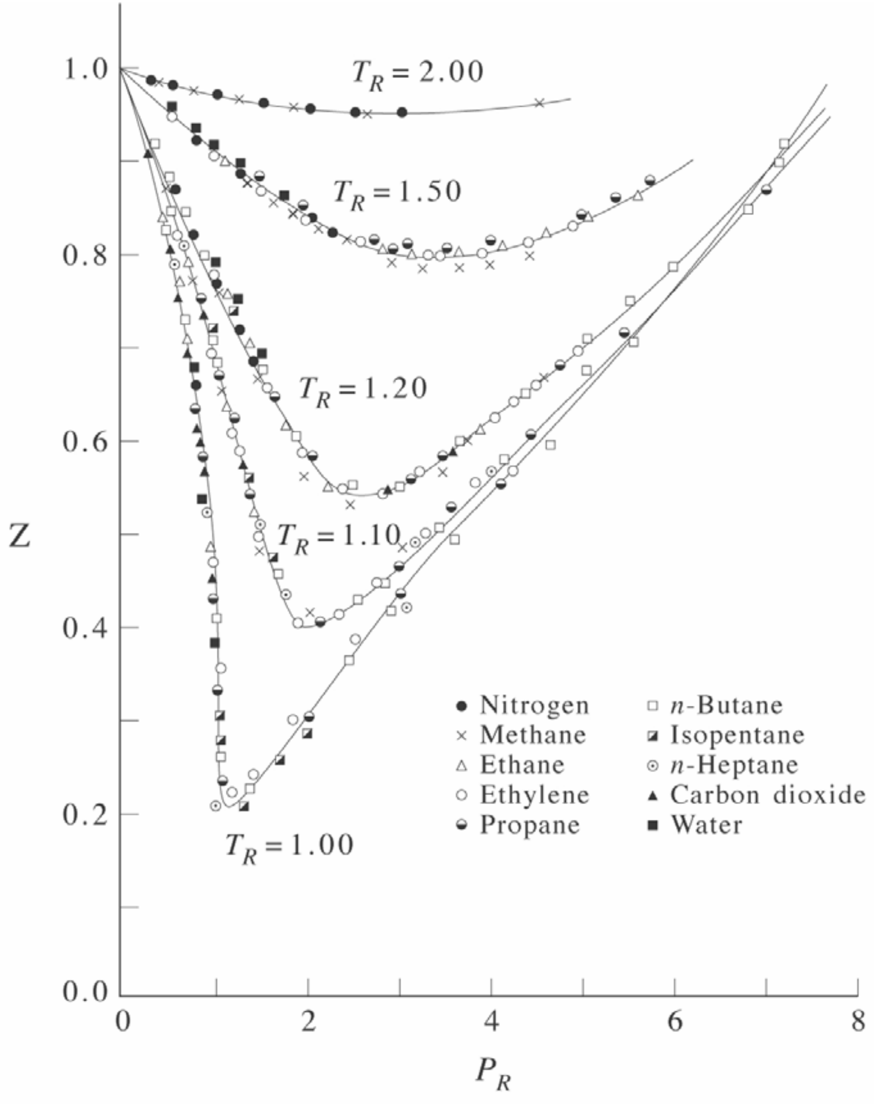
Let… $\overline{V}_R = \dfrac{\overline{V}}{\overline{V}_c}$, $T_R = \dfrac{T}{T_c}$, and $P_R = \dfrac{P}{P_c}$ to get:

$$\left(P_R + \frac{3}{\overline{V}_R^{\,2}}\right)\left(\overline{V}_R - \frac{1}{3}\right) = \frac{8}{3}T_R$$

Universal equation for *all* gases!

Law of Corresponding States The properties of all gases are the same if we compare them under the same conditions relative to their critical point.

Law of Corresponding States



The compressibility factor also obeys the LOCS. So *Z* has the same functional form for *all* gases at the corresponding conditions.

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

A gas "knows" its critical temperature, and is therefore "aware" of its temperature *relative* to its critical temperature ($T_R = T/T_c$).

Virial Expansion

Express the compressibility as an (infinite) series of terms to get an exact expression (more of a statistical model).

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

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

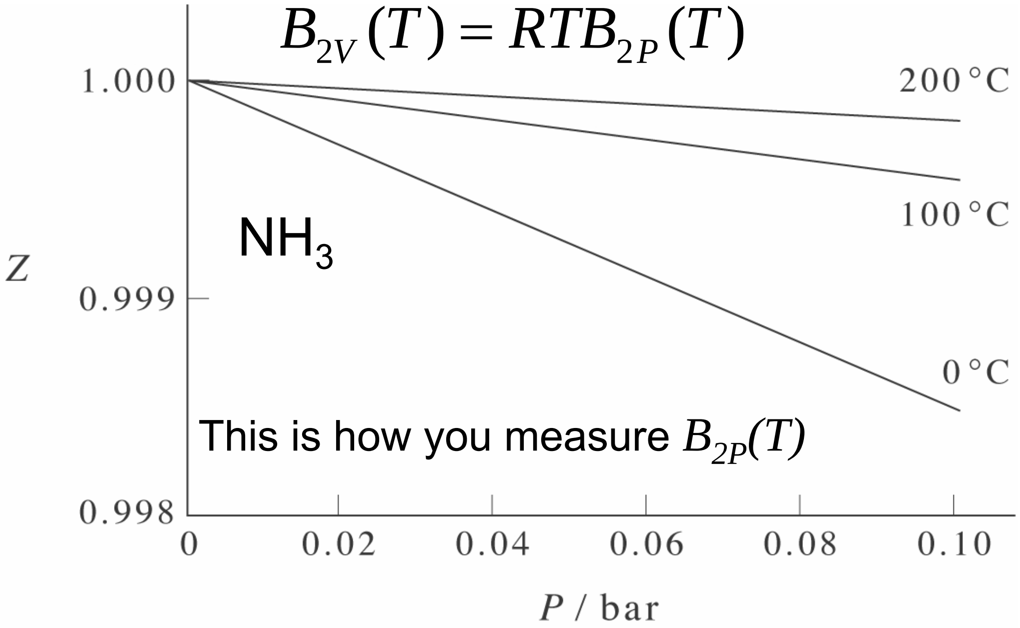
B_{nV} are virial coefficient (e.g., B_{2V} is the second virial coefficient)

As the molar volume becomes large or the pressure becomes small…

$$Z = ??$$

2nd Virial Coefficient

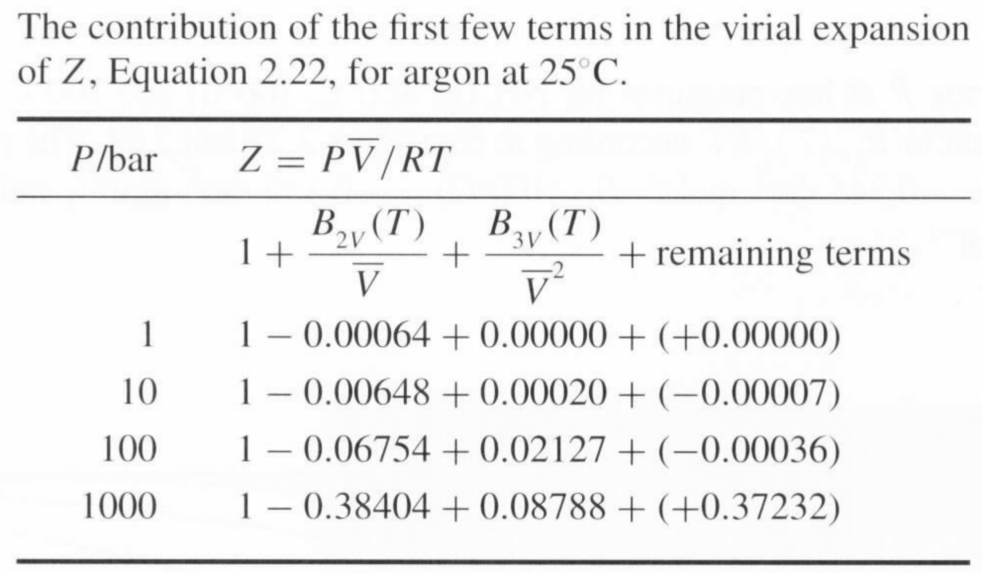
The second virial coefficient is the first deviation from ideality (as a result of *intermolecular interactions*) as the pressure is increased (or molar volume is decreased).



$$B_{2V}(T) = RTB_{2P}(T)$$

This is how you measure $B_{2P}(T)$

TABLE 2.6



The contribution of the first few terms in the virial expansion of Z, Equation 2.22, for argon at 25°C.

P/bar	$Z = P\overline{V}/RT$
	$1 + \frac{B_{2V}(T)}{\overline{V}} + \frac{B_{3V}(T)}{\overline{V}^2}$ + remaining terms
1	$1 - 0.00064 + 0.00000 + (+0.00000)$
10	$1 - 0.00648 + 0.00020 + (-0.00007)$
100	$1 - 0.06754 + 0.02127 + (-0.00036)$
1000	$1 - 0.38404 + 0.08788 + (+0.37232)$

For ammonia…

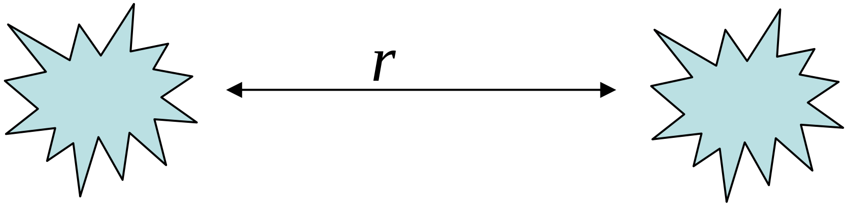
B_{2V} (0 °C) = -0.345 $dm^3 \cdot mol^{-1}$

B_{2V} (100 °C) = -0.142 $dm^3 \cdot mol^{-1}$

B_{2V} (2000 °C) = -0.075 $dm^3 \cdot mol^{-1}$

Molecules “Feel” Each Other

The virial expansions can be used to derive exact relationships between the virial coefficients and intermolecular interactions.



Consider 2 molecules and assume that their interaction depends only on how close they are to one another (r), the B_{2V} can be expressed as:

$$B_{2V}(T) = -2\pi N_A \int_0^\infty \left[e^{\frac{-u(r)}{k_B T}} - 1 \right] r^2 dr$$

If $u(r)=0$ (no intermolecular interactions) what does B_{2V} equal?

u(r), the interaction potential

“From principle $u(r)$ can be calculated from quantum mechanics, but this is a difficult computational problem.” McQuarrie and Simon, pg.

$$u(r) \rightarrow -\frac{c_6}{r^6}$$

Attraction potential

$$u(r) \rightarrow \frac{c_{12}}{r^{12}}$$

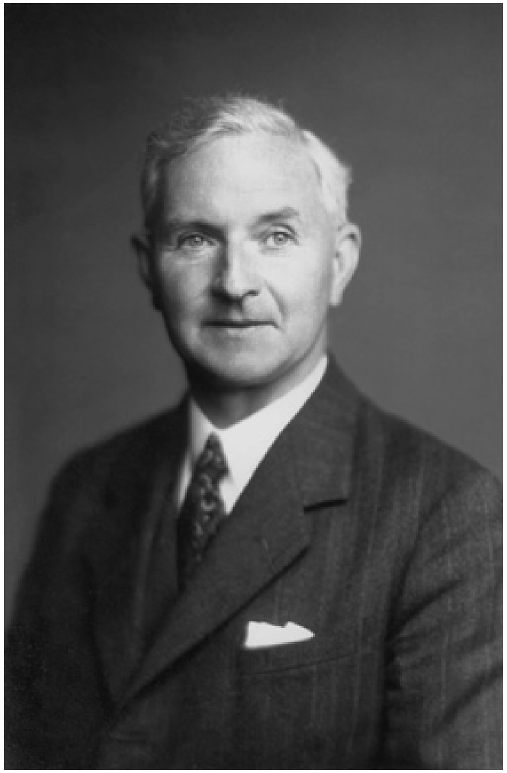
Repulsion potential

The attraction potential is valid for large *r*, but the repulsion potential operates at large *r*.

Add them up:

$$u(r) = -\frac{c_6}{r^6} + \frac{c_{12}}{r^{12}}$$

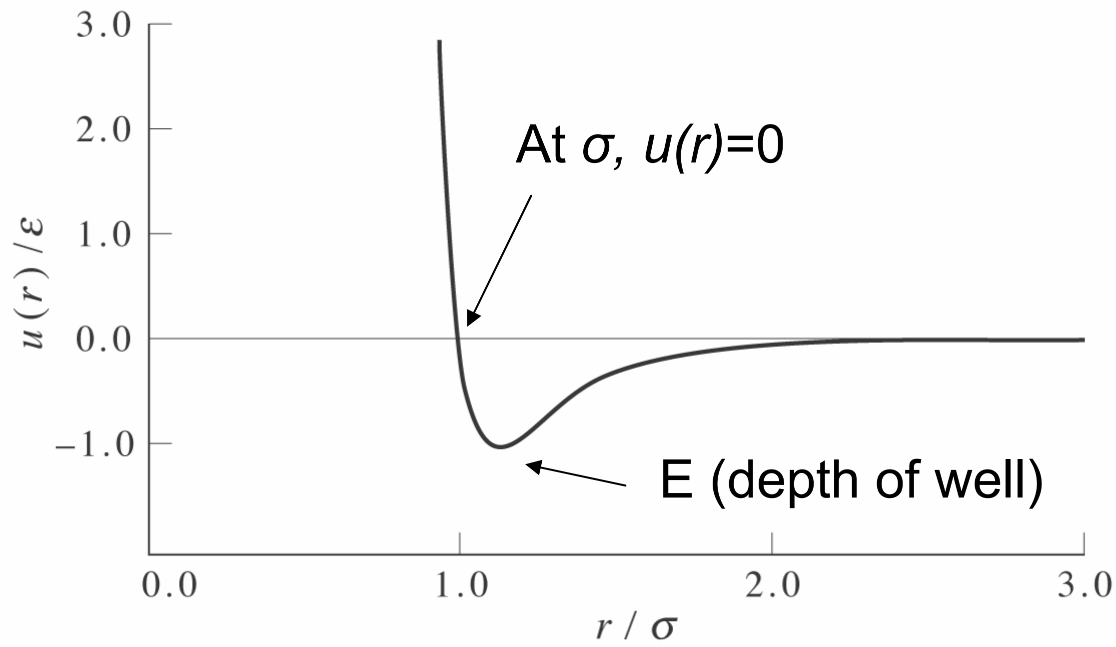
Lennard-Jones Potential



John Lennard-Jones

$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$c_{12} = 4\varepsilon\sigma^{12} \qquad c_6 = 4\varepsilon\sigma^{6}$$



At σ, u(r)=0

E (depth of well)

L-J parameters are used to calculate fluid properties such as viscosity, thermal conductivity, heats of vaporization, and crystal properties.

The L-J Data

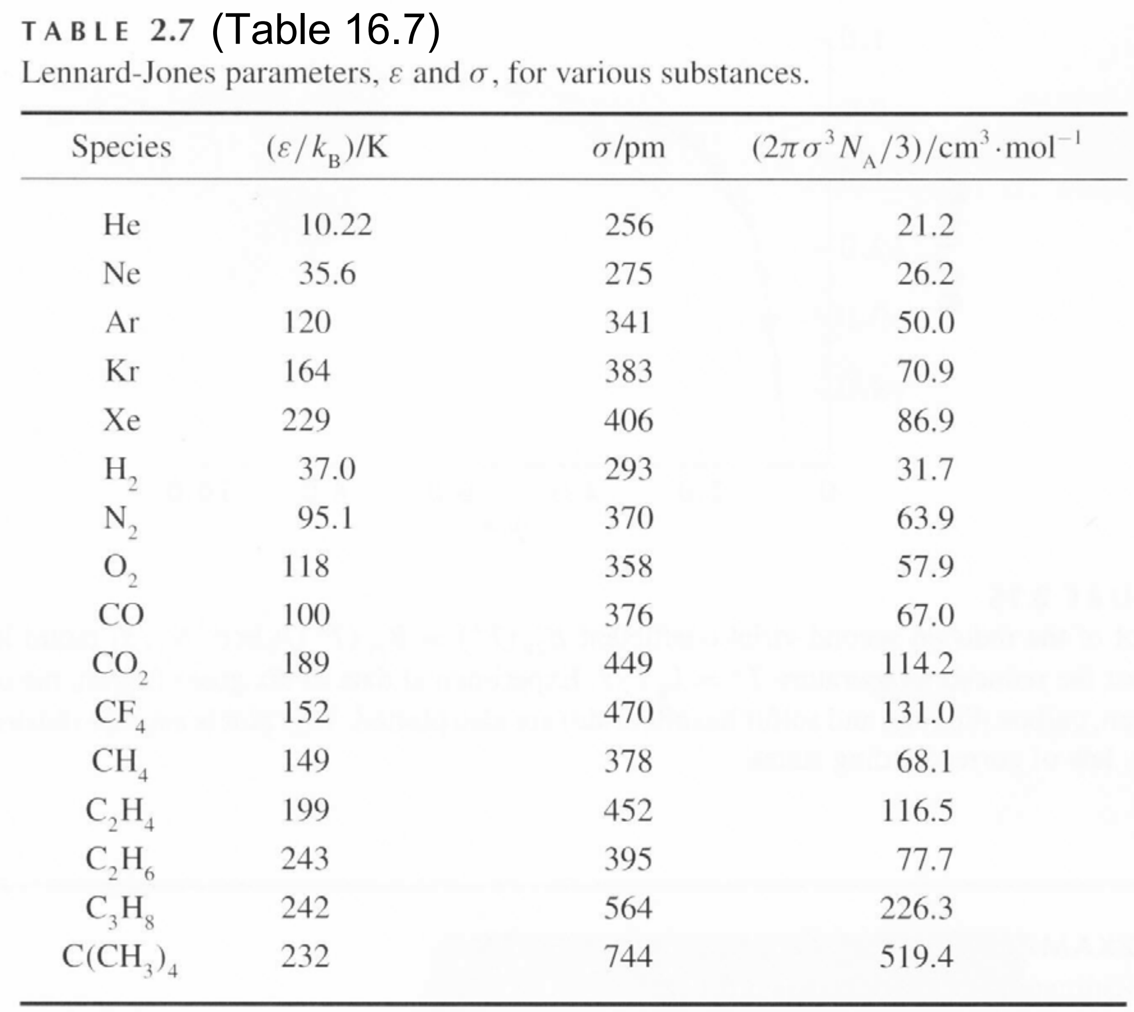


TABLE 2.7 (Table 16.7)

Lennard-Jones parameters, ε and σ, for various substances.

Species	(ε/k_B)/K	σ/pm	$(2\pi\sigma^3 N_A/3)/\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$
He	10.22	256	21.2
Ne	35.6	275	26.2
Ar	120	341	50.0
Kr	164	383	70.9
Xe	229	406	86.9
H_2	37.0	293	31.7
N_2	95.1	370	63.9
O_2	118	358	57.9
CO	100	376	67.0
CO_2	189	449	114.2
CF_4	152	470	131.0
CH_4	149	378	68.1
C_2H_4	199	452	116.5
C_2H_6	243	395	77.7
C_3H_8	242	564	226.3
$C(CH_3)_4$	232	744	519.4

ε is an energy σ is a length

How does B_{2v} relate to ε and σ?

$$B_{2V}(T) = -2\pi N_A \int_0^\infty \left[\exp\left\{ -\frac{4\varepsilon}{k_B T}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \right\} - 1 \right] r^2 dr$$

Substitute:

$x = r/\sigma$ and $T^* = k_B T/\varepsilon$

$$B_{2V}(T^*) = -2\pi\sigma^3 N_A \int_0^\infty \left[\exp\left\{ -\frac{4}{T^*}\left[(x)^{-12} - (x)^{-6} \right] \right\} - 1 \right] x^2 dx$$

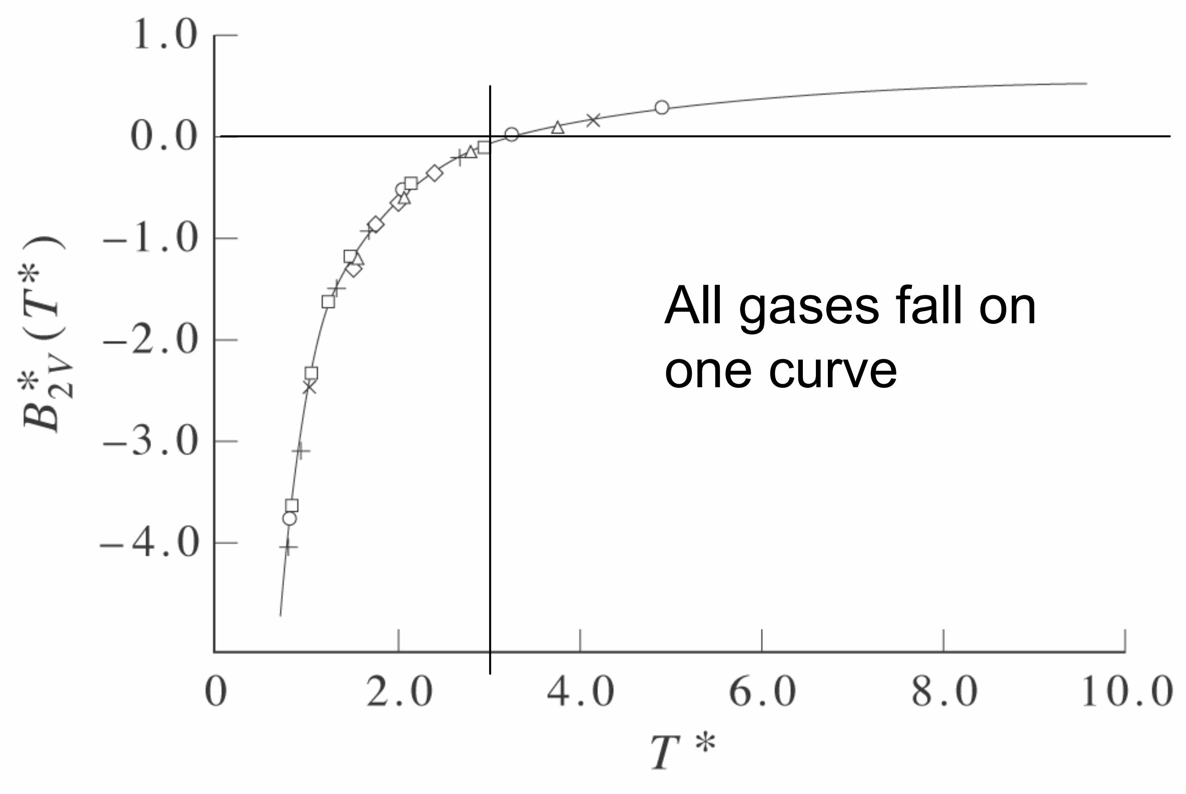
Substitute: $B^*_{2V}(T^*) = \dfrac{B_{2V}(T^*)}{\frac{2}{3}\pi\sigma^3 N_A}$

$$\boxed{B^*_{2V}(T^*) = -3\int_0^\infty \left[\exp\left\{ -\frac{4}{T^*}\left[(x)^{-12} - (x)^{-6} \right] \right\} - 1 \right] x^2 dx}$$

This expression needs to be evaluated numerically; luckily, tables of $B_{2V}^*(T^*)$ vs T^* are available.

Another LOCS Example

Plotting $B_{2V}^{*}(T^{*})$ vs. T^* yields another example of law of corresponding states



All gases fall on one curve

Note: Typically, L-J parameters are determined from experimental B_{2V} values.

At $T^* \sim 3.2$, $B_{2V}(T^*) = 0$

How does a gas act at this temperature (called the Boyle temperature)?

A simple interpretation of B_{2V}

Under conditions where we can ignore terms in P^2 and higher…

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

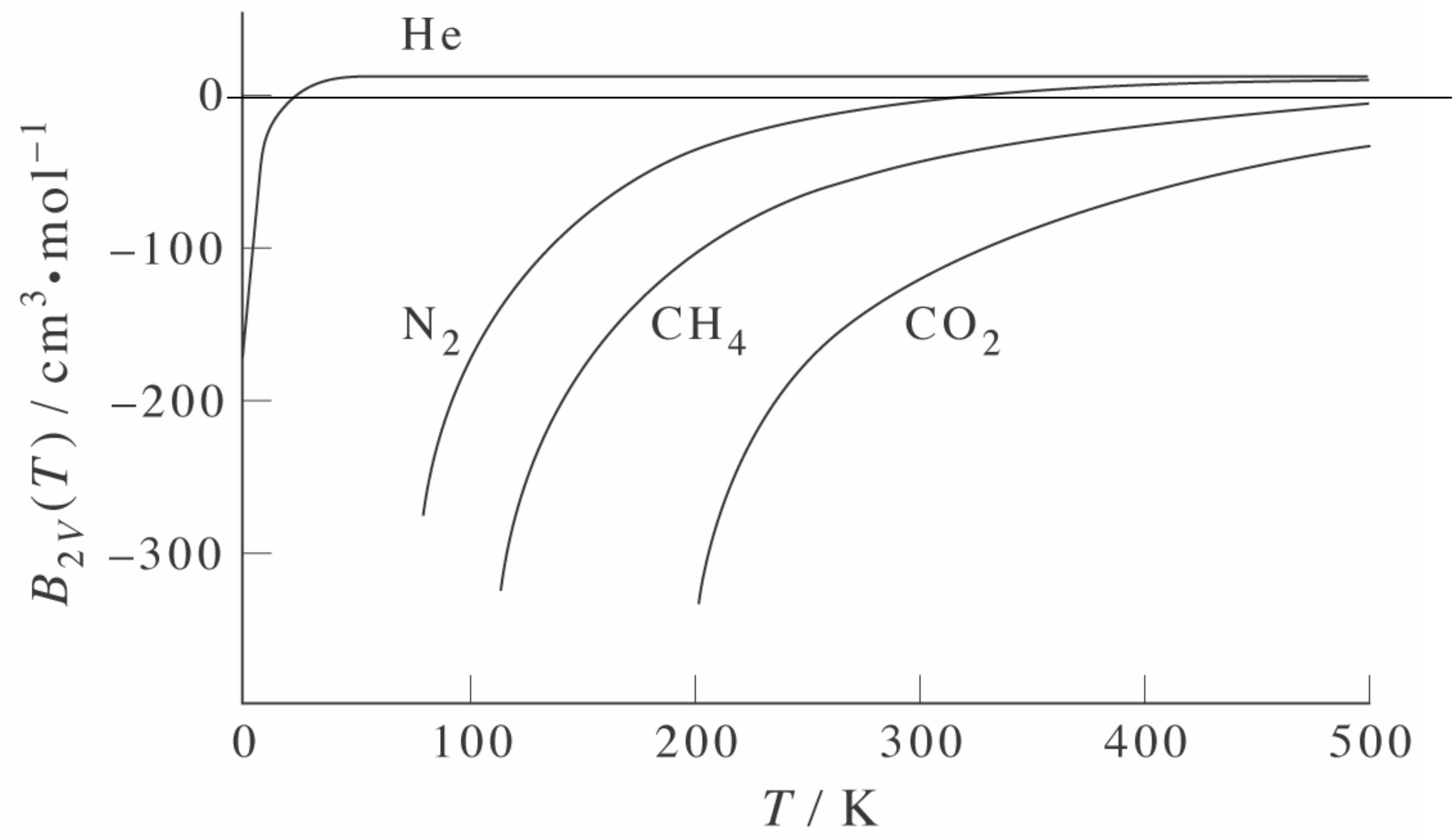
Multiply by RT/P and let $\overline{V}_{ideal} = \frac{RT}{P}$ …

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

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

B_{2V} is the difference between the actual value of the molar volume and the ideal gas value!

$B_{2V}(T)$ as a function of T and ID



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

Why do these plots look this way?

Understanding Attraction

The repulsive term of the L-J potential (the r^{-12} term) is not quite fully understood, but the r^{-6} attraction term is understood…

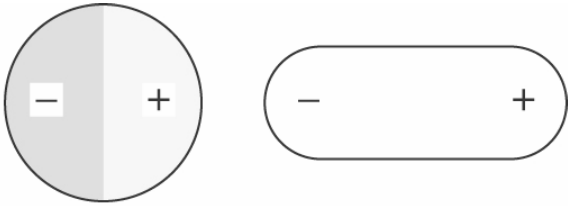
Dipole interactions

(a)

$$u_{d,d}(r) = -\frac{2\mu_1^2\mu_2^2}{(4\pi\varepsilon_0)(3k_BT)}\frac{1}{r^6}$$

(b)

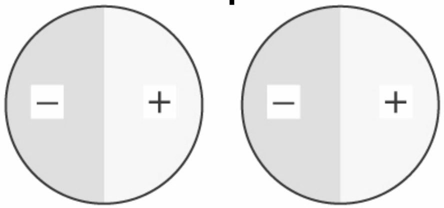
Induced Dipole-Dipole interactions



(c)

$$u_{induced}(r) = -\frac{\mu_1^2\alpha_2}{(4\pi\varepsilon_0)r^6} - \frac{\mu_2^2\alpha_1}{(4\pi\varepsilon_0)r^6}$$

Induced Dipole interactions

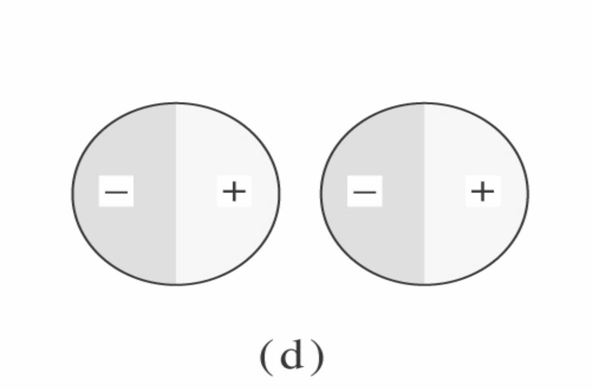


(d)

$$u_{disp}(r) = -\frac{3}{2}\left(\frac{I_1I_2}{I_1+I_2}\right)\frac{\alpha_1\alpha_2}{(4\pi\varepsilon_0)^2}\frac{1}{r^6}$$

London dispersion interactions

Only intermolecular force for non-polar molecules. How can we understand this?



(d)

The electrons from one *polarizable* atom can not completely shield the + charge of the nucleus from another *polarizable* atom.

This results in distortion of the electronic wave function and an overall lowering of the energy.

Ionization energy (J)

Polarizability (C·m^2·V^{-1})

Non-identical molecules

$$u_{disp}(r) = -\frac{3}{2}\left(\frac{I_1 I_2}{I_1 + I_2}\right)\frac{\alpha_1 \alpha_2}{(4\pi\varepsilon_0)^2}\frac{1}{r^6}$$

Permittivity of vacuum (C^2·J^{-1}·m)

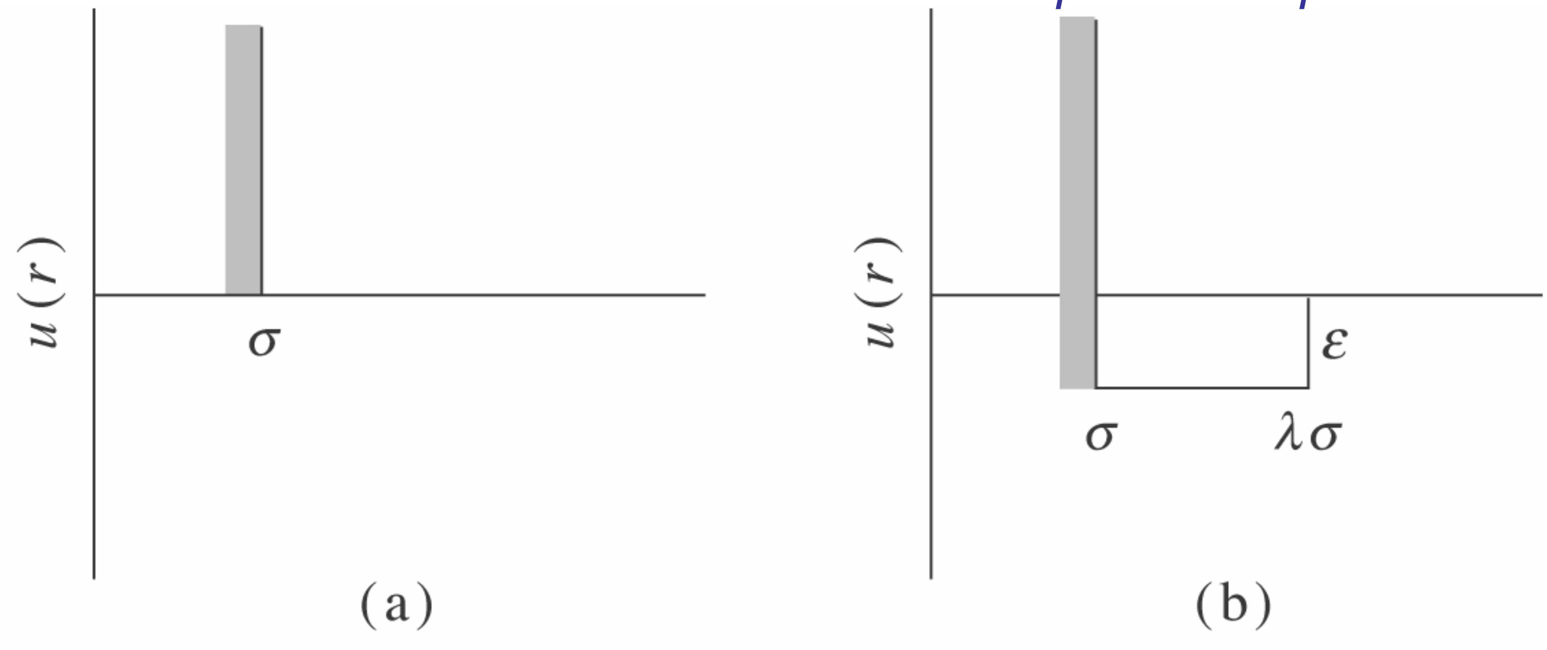
Identical molecules

L-J is nice, but hard to use!

Isn't there an analytical solution for $u(r)$?
Yes, but we have to resort to simple models…

Hard-sphere potential

Square-well potential



$$u(r<\sigma)=\infty$$
$$u(r>\sigma)=0$$

$$u(r<\sigma)=\infty$$
$$u(\sigma<r<\lambda\sigma)=-\varepsilon$$
$$u(r>\lambda\sigma)=0$$

Solution for hard sphere model

No attractive term! Good only at high T (with respect to ε/k_B).

$$B_{2V}(T) = -2\pi N_A \int_0^{\infty} \left[e^{\frac{-u(r)}{k_B T}} - 1 \right] r^2 dr$$

$$= -2\pi N_A \int_0^{\sigma} \left[e^{\infty} - 1 \right] \ r^2 dr - 2\pi N_A \int_{\sigma}^{\infty} \left[e^{0} - 1 \right] \ r^2 dr$$

$$= \frac{2\pi\sigma^3 N_A}{3}$$

This expression is 4 times the volume of N_A spheres and σ can be thought of as the sphere diameter.

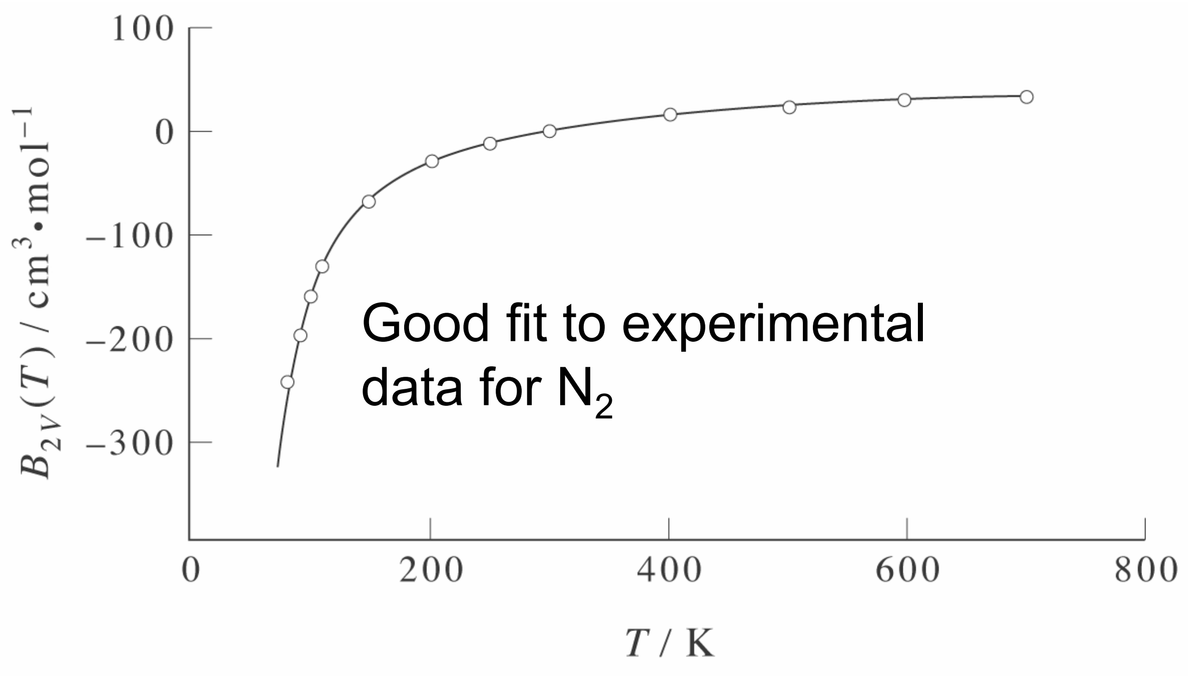
Independent of T, but remember… this expression is only valid for high T!

Solution for square well model

$$B_{2V}(T) = \frac{2\pi\sigma^3 N_A}{3}\left[1-\left(\lambda^3-1\right)\left(e^{\varepsilon/k_BT}-1\right)\right]$$

What are the steps to get this answer?

What happens at λ = 1 or ε = 0?



Good fit to experimental data for N_2

	sqwm	L-J
σ (pm)	328	370
ε/k_B (K)	95.2	95.1
λ	1.58	N/A

Summary I

1. Gases are rarely ideal (PV=nRT fails miserably!).
2. van der Waals came up with an equation of state to account for non-idealities.
3. Cubic equations of state describe both the liquid and gaseous regions of the P-V isotherms.
4. At the critical point, VDW EOS has only one real root. Remember why this is important?!? (Hint: Think about a, b, and the critical values.)
5. The law of corresponding states says that all gases have the same properties if compared at corresponding conditions.

Summary II

6. The virial expansion is in ways better than the VDW EOS.
7. The second virial coefficient is the most important and can be used to relate the properties of gases to molecular interactions.
8. Lennard-Jones came up with an expression for $u(r)$ in terms of the strength of molecular interactions (ε) and their size (σ).
9. LJ parameters come from experimental B_{2V} values.
10. London dispersion interactions can be understood through quantum mechanics.
11. Simple models (e.g., square well potential) can be used effectively to get molecular information about gases.