*Real Gases and the van der Waals Equation

By Shawn P. Shields, Ph. D.

Real Gases…What are they?

- Most gases behave ideally when they are held at low pressures and “high” temperatures.

(Room temperature is considered high T.)

- Remember that “ideal behavior” means that the gas molecules do not interact with each other. Only kinetic energy is present.

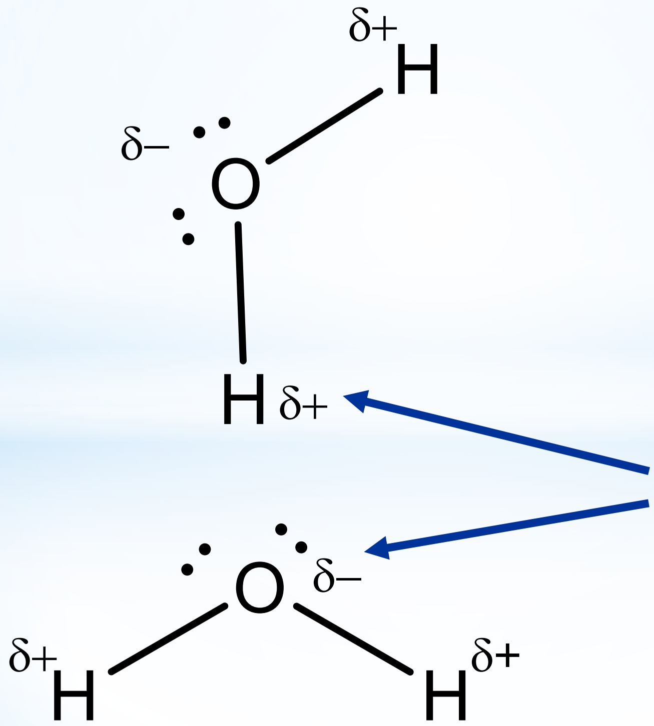
* Real Gases…What are they?

* However, sometimes gas molecules DO interact with each other.
* Interactions between gas molecules is more likely at
  * **low temperatures**
  * **high gas pressures** (i.e., high gas densities).

This introduces potential energy into the picture!

* Real Gases…What are they?

* **Molecules that have significant intermolecular attractions (aka "polar" molecules)** may also interact with each other.



Water is a polar molecule.

"partial charges" on the molecules are attracted to each other

The Compressibility Factor, Z

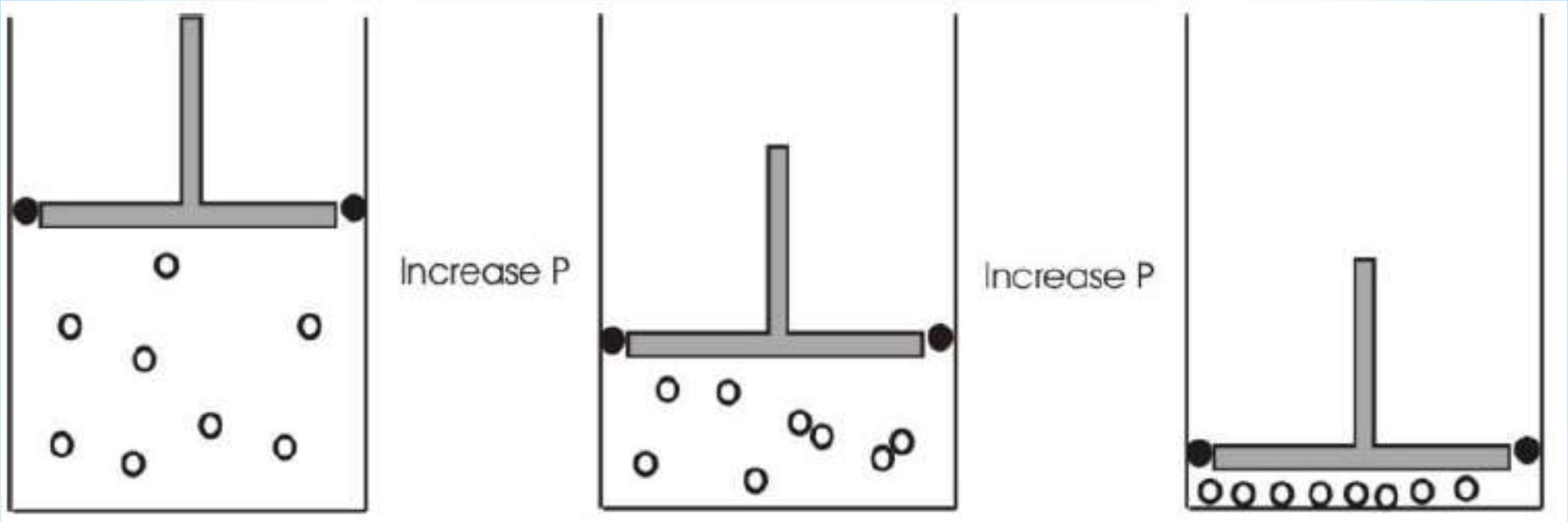
* We can use the "compressibility factor" (Z) to detect deviations of a gas from ideal behavior in experiments.

$$Z = \frac{PV}{nRT}$$

* When Z < 1, intermolecular attractions exist, and gas molecules can "feel" each other's presence. ☺

*Real Gas Behavior

Compare 3 scenarios for gases in a piston…



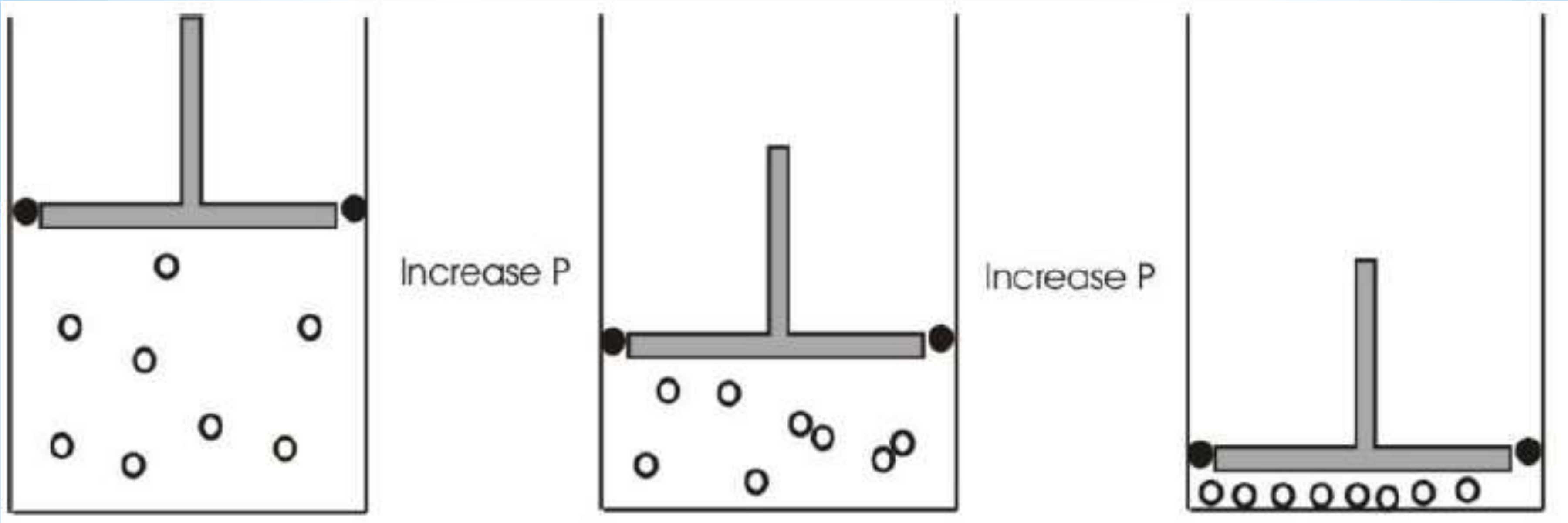
Low P

The first piston shows a gas at low pressure.

$$V_{actual} = V_{ideal}$$

Ideal Gas Law and KTG are obeyed. ☺

*Real Gas Behavior



Med to high P

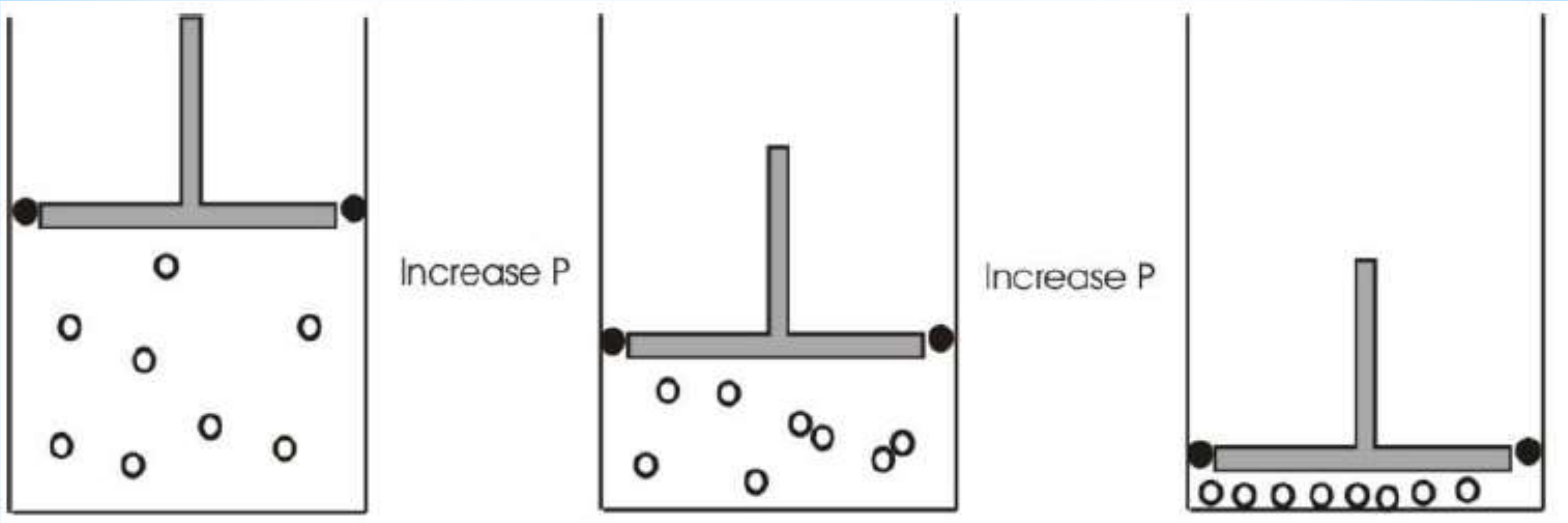
The second piston shows a gas at med-high pressure. As the volume decreases, some molecules stick together, effectively *reducing the moles of gas.*

Now, $V_{actual} < V_{ideal}$

The *gas* is <u>more compressible</u>, and *attractions* dominate!

* Real Gas Behavior

Compare 3 scenarios for gases in a piston…



Ridiculously high P

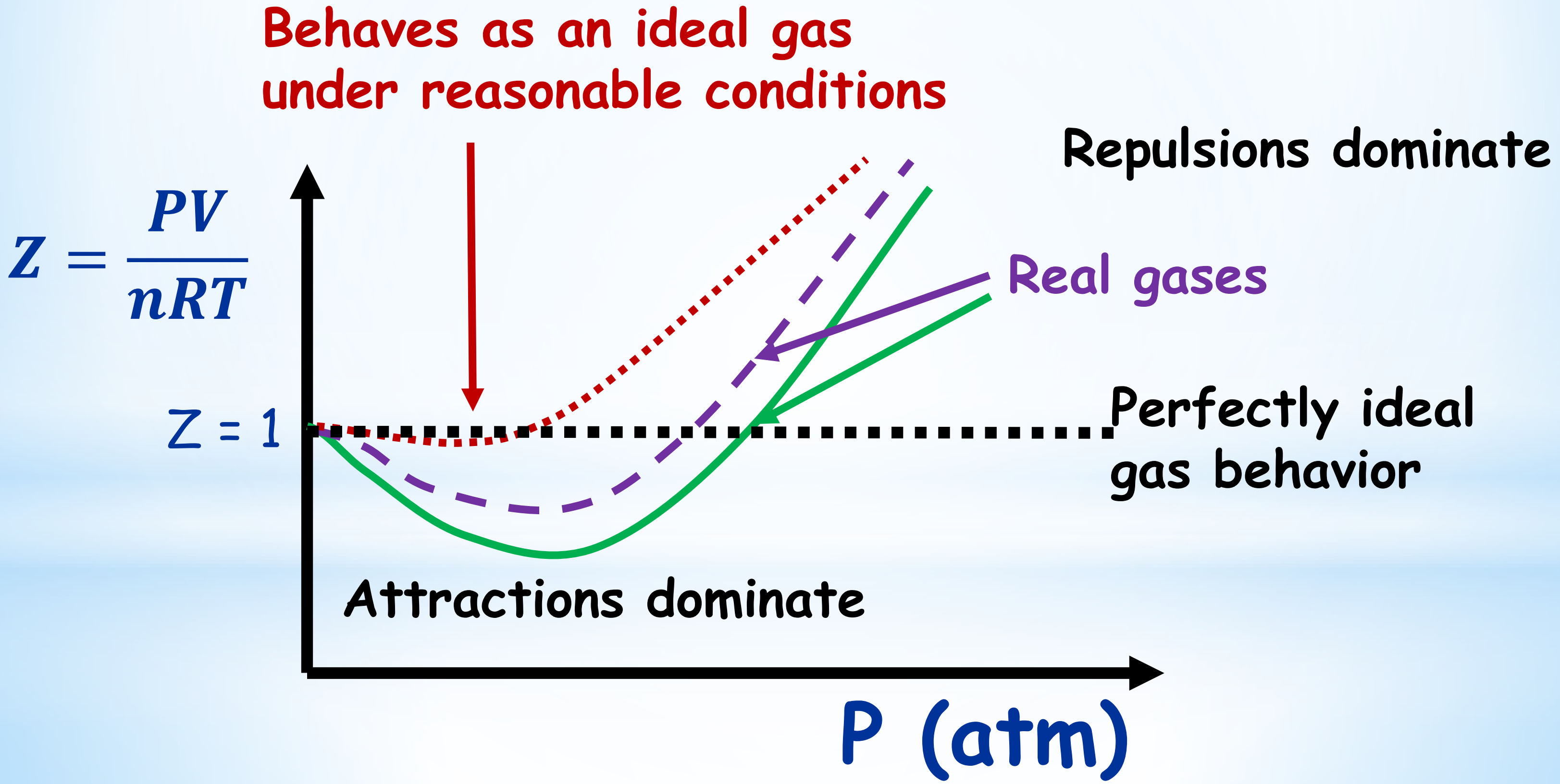
The third piston shows a gas at REALLY high pressure.

The gas cannot move and we see that it actually DOES take up space…as our common sense might tell us.

Now, $V_{actual} > V_{ideal}$ Repulsions dominate!

*The Compressibility Factor, Z

* More about the compressibility factor Z



* The van der Waals Equation

* Corrects the Ideal Gas Law for real gas behavior.

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

* The van der Waals constants a and b are experimentally-determined for each individual gas.
* The vdw **constant a** describes the strength of attractions with units L^2 atm $mole^{-2}$
* The vdw **constant b** increases with increasing molecular size with units L mol^{-1}

* The van der Waals Equation

* Corrects the Ideal Gas Law for real gas behavior.

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Correction for the volume taken up by the gas molecules

Correction for the attractions between gas molecules. The **actual pressure P is reduced by this amount** compared to the Ideal Gas law.

* The van der Waals Equation

* Predict the relative size of the van der Waals constants for the following gases:

H_2 gas (very small and not polar)

SO_2 gas (larger atoms and polar)

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

* The van der Waals Equation

* Predict the relative size of the van der waals constants for the following gases:

H_2 gas (very small and not polar)

SO_2 gas (larger atoms and polar)

The vdw constant a and b would both be larger for SO_2 gas.

* The van der Waals Equation

* Which gas would produce the lowest pressure, with moles, T and V constant?

CH_4 (methane) gas
(small molecule and not polar)

H_2O gas
(small molecules and polar)

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

*The van der Waals Equation

* Which gas would produce the lowest pressure, with moles, T and V constant?

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

If CH_4 is a small molecule, and not polar, this means that a and b are both relatively small. (a = 2.25, b = 0.0428)

The gas should behave close to ideally.

If H_2O gas is also a small molecule, then the vdw constant b will be of a similar size. However, since water is polar, the vdw constant a will be quite a bit larger.
(a = 5.46, b = 0.0305)

The pressure exerted by water will be lower than the ideal pressure.

* Summary

* Real gases interact with each other and take up volume in the container.

* The van der Waals equation corrects the Ideal Gas Law for real gas behavior.

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

If the gas is under ideal gas conditions, the van der Waals equation reduces to the Ideal Gas Law PV=nRT

(Try this by making a and b = 0) ☺