

5.7 The Kinetic Molecular Theory of Gases (KMT)

Gas laws predict properties of gases but do not explain why they behave as they do. Discussion in 5.6 (read!) explains how the effects on a gas are understood in terms of the Kinetic Molecular Model. Most important to this discussion is temperature.

Temperature: “A measure of the average kinetic energy of the particles”, or an index of the random motion of the particles; i.e. higher temperature, greater motion.

Kinetic Energy is derived as: $KE_{(avg)} = \frac{1}{2}mv^2 = \frac{1}{2}m\overline{v^2} = (App.2) = \frac{3}{2}RT$ ($R = 8.3145 \text{ J/mol K}$)

Root Mean Square Velocity: The average of the squares of particle velocities, $\overline{v^2}$ (from $\frac{1}{2}mv^2$)

$u_{rms} = \sqrt{\overline{v^2}}$, root mean square velocity, “average speed of particle”

$$u_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3RT}{M}} = \text{m/s units}$$

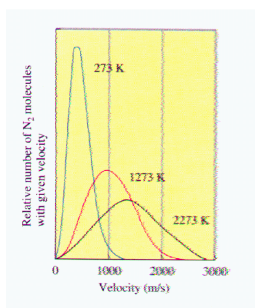
M = molar mass in kg/mol

R = 8.3145 J/K · mol

Ex. Calculate u_{rms} of He at 25°C. (1300 m/s)

Predict the speed of a molecule that is 2 times heavier than He. (slower, but not $\frac{1}{2}$ the speed. It would be slower by $\sqrt{2}$, or 960 m/s.

Are all gases moving at this speed? Yes, but only for a very short distance until they collide with another gas molecule. The mean free path is the average distance a molecule travels between collisions. Very small distance. A range of velocities is *observed due to collisions amongst particles* which slows the mixing process. At higher temperatures, the curve's peak moves toward the higher value and the range of the velocities becomes greater. See figure below (Zumdahl: 4th edition, Houghton Mifflin Press)



5.8 Effusion and Diffusion of Gases

Diffusion: refers to the mixing of gases, a complicated treatment.

Effusion: Passage of a gas through a tiny orifice into an evacuated chamber. Rate (speed) in ml/min is measured here.

Thomas Graham's Law of Effusion: (at same temperature and pressure)

The rate of effusion is inversely proportional to the square roots of the molecular mass.

$$\frac{u_{rms1}}{u_{rms2}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

Compare's the rate of effusion.

Ex. Under a set of conditions, SO₂ gas (64 g/mol) effuses at 24 ml/min. What rate would O₂ gas (32 g/mol) effuse?

Ans: O₂ gas is lighter and is predicted to travel faster, but only $\sqrt{2}$ x faster. Compare correctly 34 ml/min, not 48 ml/min.

5.9 Real Gases

Real gases deviate from ideal behavior. Real gases approach ideal behavior at conditions of high temperature and low pressure.

Ideal Gas:

- Point mass, no volume because the distances between particles is so great that it is assumed that their volumes are negligible. In reality, the volumes of the gas particles do occupy space of the container.
- The average kinetic energy of the particles is directly proportional to the absolute temperature.
- Gas particles are independent of each other. Identities of particles do not matter since volume is unimportant.
- Particles are in constant motion. Collisions create pressure. Collisions are elastic which is to say that no energy is lost.
- No intermolecular attractions or repulsions. H₂O vapor is a terrible ideal gas.
- $\frac{PV}{nRT} = 1$

van der Waals Equation: Modified ideal gas equation for real gases.

- First, account for the finite volumes of gas. Gases do occupy volume of the container.
V-nb, where n is the number of moles and b is an empirical constant. See Table 5.3

$$P' = \frac{nRT}{(V - nb)} \quad \text{note: as the value of } b \text{ increases, so does the size of particle.}$$

- Second, account for the intermolecular attractions. The real effect of this is to make the pressure *lower*. This is affected by the concentration of molecules, (n/V), and is less significant at higher temperatures in which the particles are moving faster and will not apply an attractive or repulsive force on each other.

$$P_{\text{obs}} = \frac{nRT}{(V - nb)} - a\left(\frac{n}{V}\right)^2$$

note: the value of a increases with amount of intermolecular attractions.

van der Waals equation:

$$\left[P_{\text{obs}} + a\left(\frac{n}{V}\right)^2 \right] (V - nb) = nRT$$

Homework Practice:

P. 219 #26, 77, 79, 80, 81, 82, 83, 84, 85, 86, 90, 124, 129

VAN DER WAALS EQUATION OF STATE

<http://www.ac.wvu.edu/~vawter/PhysicsNet/Topics/Thermal/vdWaalEquatOfState.html>

- The [Ideal Gas Law](#), $PV = nRT$, can be derived by assuming that the molecules that make up the gas have negligible sizes, that their collision with themselves and the wall are perfectly elastic, and that the molecules have no interactions with each other.
- The van der Waal's equation is a second order approximation of the equation of state of a gas that will work even when the density of the gas is not low.

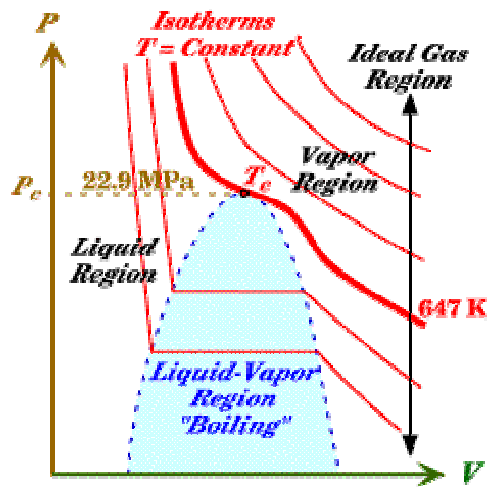
$$\left(P + a \left(\frac{n}{V} \right)^2 \right) (V - nb) = nRT$$

- Here **a** and **b** are constants particular to a given gas.

Some van der Waals Constants

| Substance | a (J m ³ /mole ²) | b (m ³ /mole) | P_c (MPa) | T_c (K) |
|--|--|------------------------------------|-------------------------------|-----------------------------|
| Air | .1358 | 3.64x10 ⁻⁵ | 3.77 | 133 K |
| Carbon Dioxide (CO ₂) | .3643 | 4.27x10 ⁻⁵ | 7.39 | 304.2 K |
| Nitrogen (N ₂) | .1361 | 3.85x10 ⁻⁵ | 3.39 | 126.2 K |
| Hydrogen (H ₂) | .0247 | 2.65x10 ⁻⁵ | 1.30 | 33.2 K |
| Water (H ₂ O) | .5507 | 3.04x10 ⁻⁵ | 22.09 | 647.3 K |
| Ammonia (NH ₃) | .4233 | 3.73x10 ⁻⁵ | 11.28 | 406 K |
| Helium (He) | .00341 | 2.34x10 ⁻⁵ | 0.23 | 5.2 K |
| Freon (CCl ₂ F ₂) | 1.078 | 9.98x10 ⁻⁵ | 4.12 | 385 K |

- The parameter **b** is related to the size of each molecule. The volume that the molecules have to move around in is not just the volume of the container **V**, but is reduced to (**V - nb**).
- The parameter **a** is related to intermolecular attractive force between the molecules, and **n/V** is the density of molecules. The net effect of the intermolecular attractive force is to reduce the pressure for a given volume and temperature.
- When the density of the gas is low (i.e., when **n/V** is small and **nb** is small compared to **V**) the van der Waals equation reduces to that of the ideal gas law.
- One region where the van der Waals equation works well is for temperatures that are slightly above the critical temperature **T_c** of a substance



- Observe that inert gases like Helium have a low value of \mathbf{a} as one would expect since such gases do not interact very strongly, and that large molecules like Freon have large values of \mathbf{b} .
 - There are many more equations of state that are even better approximation of real gases than the van der Waal equation.
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