GASES

5.1 Physical States of Matter

solid
liquid

gas
    simple: $PV = nRT$

    gases have chemistry
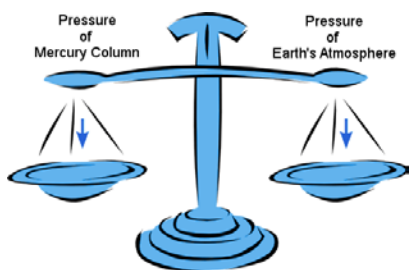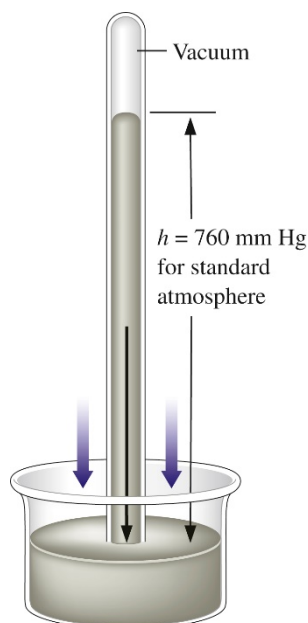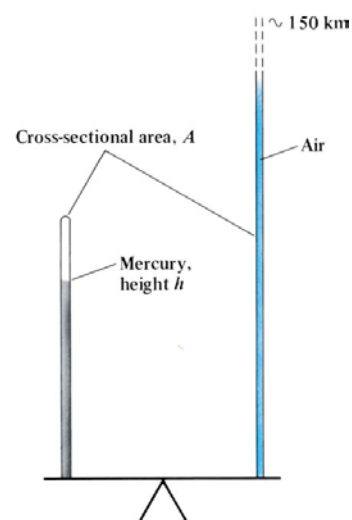
FIG I – Torricelli's Barometer

Vacuum

$h = 760$ mm Hg
for standard
atmosphere

Evangelista Torricelli, 1608-1648

~ 150 km

Cross-sectional area, A Air

Mercury,
height h

Pressure
of
Mercury Column

Pressure
of
Earth's Atmosphere

Pressure

units:
1 **atm** = 760 **torr**
    = 760 mm Hg (0°C)
    = 29.92 in Hg (0°C)
    = 101.325 kPa
    = 14.69595 psi

Units Used to Measure Pressure	
Unit Name and Abbreviation	**Definition or Equivalency**
Pascal (Pa)	$1 \text{ kg m}^{-1} \text{s}^{-2} = 1 \text{ N m}^{-2}$ (the SI unit)
Standard atmosphere (atm)	101,325 Pa exactly
Bar (bar)	100,000 Pa exactly or 0.986923 atm
Torr (torr)	(101,325/760) Pa or (1/760) atm
Millimeter of mercury at 0°C (mm Hg)	(101,325/760) Pa or (1/760) atm
Pound of force per square inch (lbf in^{-2}, or psi)	6894.757 Pa or (1/14.69595) atm

EX 1. What is the pressure when the height of a column of mercury is 76.0 crn? (d_{Hg} = 13.5951 g crn^{-3}, g = 9. 80665 rn s^{-2})

5.2 ABC Laws: Avogadro, Boyle, Charles

FIG II. Boyle's Law ($V \propto 1/P$; n, T constant)
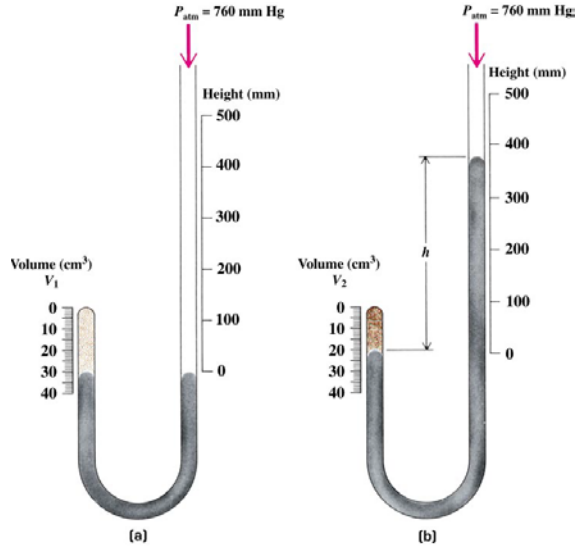
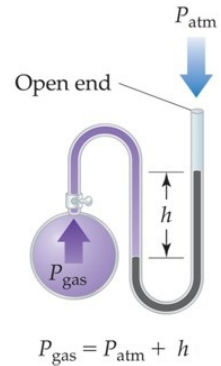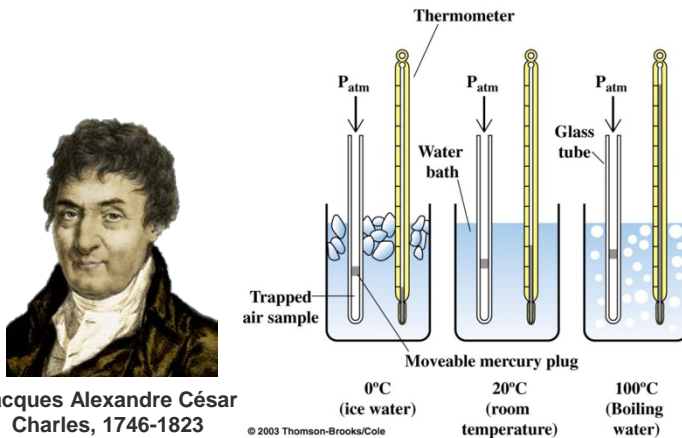**Robert Boyle, 1627-1691**

FIG III. A Manometer

$P_{gas} = P_{atm} + h$

FIG IV. Charles's Law ($V \propto T$; n, P constant)

Gay-Lussac's gas volumes

Joseph Louis Gay-Lussac, 1778-1850

Jacques Alexandre César Charles, 1746-1823

© 2003 Thomson-Brooks/Cole

Avogadro's hypothesis ($V \propto n$; T, P constant)

Lorenzo Romano Amedeo Carlo Avogadro, Count of Quaregna and Cerreto, 1776-1856

FIG V. Charles's Law Experiment for Two Gases

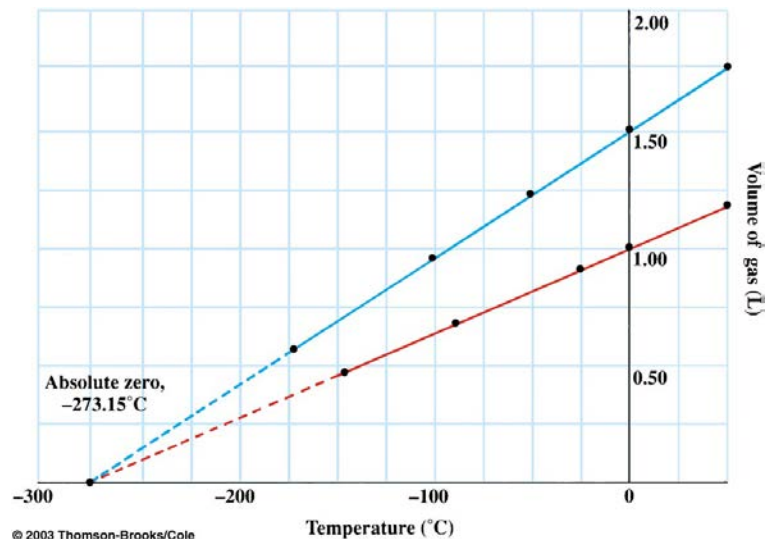$$V(t) = V_0 + \alpha V_0 t$$

where α is -1 / x-intercept. Experimentally it is found that

$$\alpha = 1 / 273.15^o C$$

so that

$$V(t) = V_0 \left[1 + \frac{t}{273.15^o C} \right]$$

where V_0 is the volume at 0°C.

© 2003 Thomson-Brooks/Cole

5.3 Ideal Gas Equation of State - $R = 0.08206$ L atm mol^{-1} K^{-1} = 8.31451 J mol^{-1} K^{-1}

EX 2. What is the volume occupied by one mole of an ideal gas at STP conditions?

EX 3. A fixed quantity of gas at 23°C has a pressure of 748 torr and occupies a volume of 10.3 L.

a) What would be the volume if the pressure is increased to 1.88 atm? (Boyle's Law)

b) What would be the volume if the temperature is increased to 165°C? (Charles's Law)

EX 4. Hydrogen fills a 250-L reaction vessel at 100°C and 1.00 atm pressure. Determine the volume of the same quantity of hydrogen at 0°C and 1.50 atm.

density and **molar** mass

EX 5. The composition of a liquid is 25.23% S and 74.77% F. It boils at 29°C where the density of the vapor is 9.95 g L^{-1} at a pressure of 738 mm Hg. What is its molecular formula?

EX 6. You have a 2-L and a 3-L flask at the same temperature. The gas in the 2-L flask has a mass of 4.8 g and that in the 3-L flask has a mass of 0.36 g. If the pressure in the 2-L flask is 10 times greater than the pressure in the 3-L flask, do the two gases have the same molar mass? If not, which contains the gas of higher molar mass?
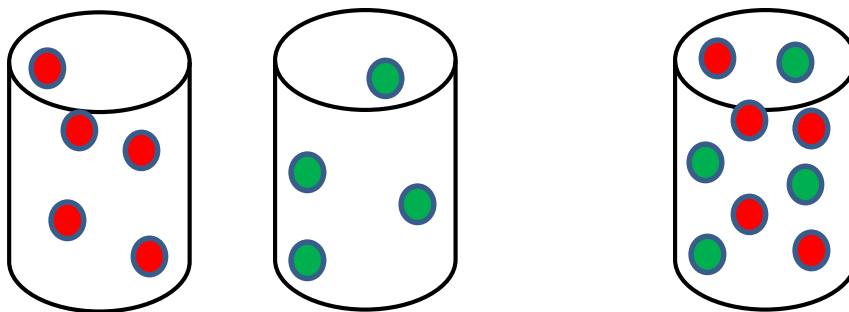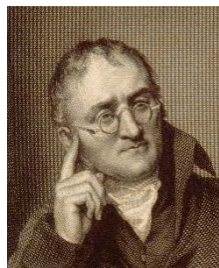

5.4 Gas Stoichiometry

EX 7. Calcium hydride (M_{CaH2} = 42.0938 g/mol) reacts with water to form hydrogen gas

$$CaH_2(s) + 2 H_2O(l) \rightarrow Ca(OH)_2(aq) + 2 H_2(g)$$
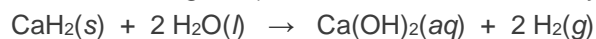
How many grams of CaH_2 are needed to generate 64.5 L of H_2 gas if the pressure of H_2 is 814 torr at 32°C?

5.5 Dalton's Law of Partial Pressure

mole fraction, X

EX 8. 0.250 mol of N_2, 0.500 mol of O_2, and 0.250 mol of CO are in a vessel at 1 atm and 25°C. The container is heated to 50°C.
a) What is the pressure of the gas mixture?

b) What is the partial pressure of O_2?

---

collecting gas over water

KClO$_3$

Oxygen plus water vapor

EX 9. 15.00 g of sodium azide is decomposed by heating and the nitrogen gas which evolves is collected over water at 25°C at a barometric pressure of 745 mm Hg. What volume of dry gas is collected if the vapor pressure of water at 25°C is 24 mm Hg?

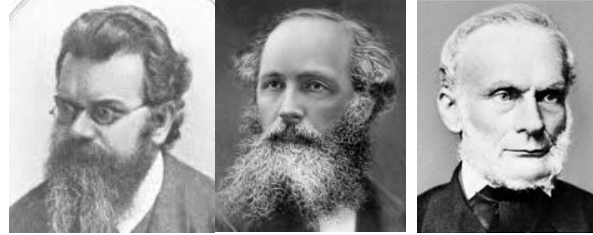$$2\ NaN_3(s)\ \rightarrow\ 2\ Na(s)\ +\ 3\ N_2(g)$$

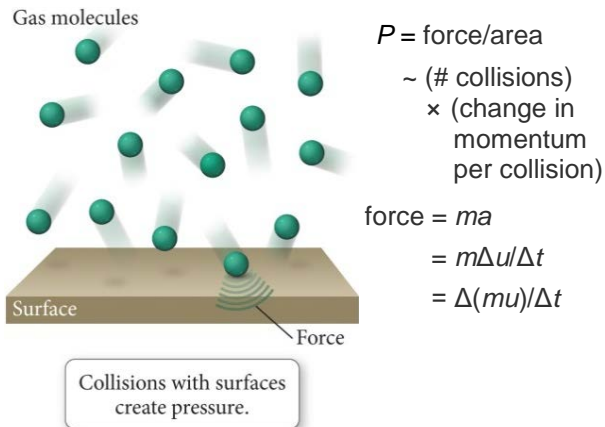## 5.6 Kinetic-Molecular Theory of Gases (Boltzmann, Maxwell, Clausius)

$PV = nRT$ - empirical, no molecular information

postulates of kinetic theory:

    molecular volume is negligible compared to distance between molecules

    large number of molecules, ceaseless random motion

    no forces of attraction or repulsion between molecules

    all collisions are elastic (no energy lost)

    Newton's laws of motion obeyed

ON A MOLECULAR LEVEL WHAT IS THE PRESSURE OF AN IDEAL GAS DUE TO?

Gas molecules

Surface

Force

Collisions with surfaces create pressure.

P = force/area

  ~ (# collisions)
    × (change in momentum per collision)

force = ma

    = $m\Delta u/\Delta t$

    = $\Delta(mu)/\Delta t$

conclusions

1. $PV = nRT = \frac{1}{3} Nm\langle u^2 \rangle$

2. $\frac{1}{2} N_o m\langle u^2 \rangle = \frac{3}{2} RT$

    | average kinetic energy (T) |

3. $\langle u^2 \rangle = 3RT/M$

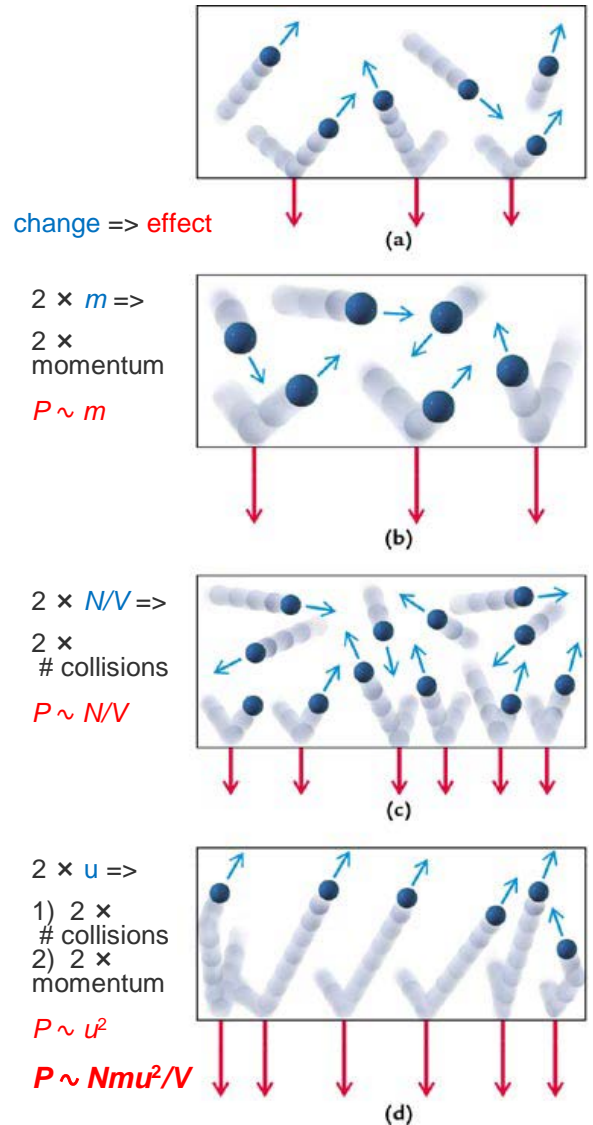root-mean-square (rms) speed = $\sqrt{\langle u^2 \rangle}$

    | $u_{rms} = \sqrt{3RT/M}$ |

(average = $\sqrt{8RT/\pi M}$; most probable = $\sqrt{2RT/M}$)

Boltzmann's constant, $k_B = R/N_0$ -->

    | $PV = nRT = Nk_B T$ |

FIG VI – Relating PV to m, u

(a)

change => effect

$2 \times m =>$
$2 \times$ momentum

$P \sim m$

(b)

$2 \times N/V =>$
$2 \times$ # collisions

$P \sim N/V$

(c)

$2 \times u =>$
1) $2 \times$ # collisions
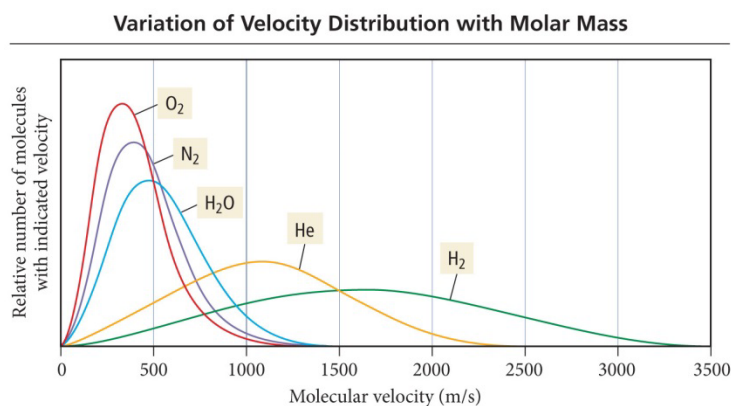2) $2 \times$ momentum

$P \sim u^2$

$P \sim Nmu^2/V$

(d)

EX 10. What is u_{rms} for helium at -73°C?

EX 11. At STP hydrogen and deuterium can be considered to be ideal gases. If $\langle u_{H2} \rangle = 1.70 \times 10^5$ cm s^{-1} at STP what is $\langle u \rangle$ for D_2?
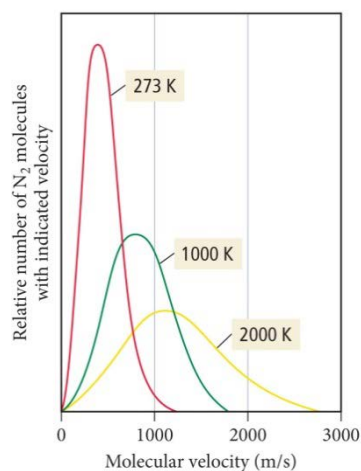
Maxwell-Boltzmann Distribution Law of Molecular Speeds

$$f(u) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} u^2 e^{-mu^2/2kT}$$

Variation of Velocity Distribution with Molar Mass

FIG VII. effect of molar mass

Variation of Velocity Distribution with Temperature
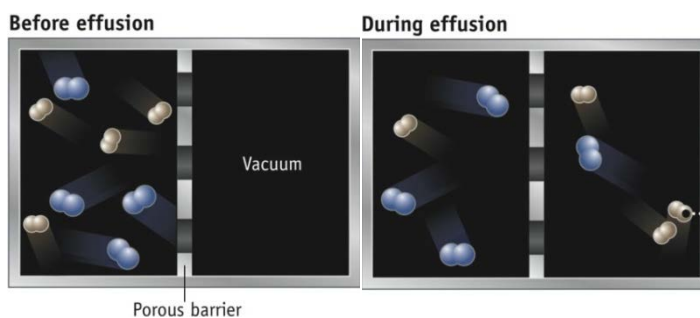
FIG VIII. effect of temperature

5.7 Graham's Law of Effusion

OBSERVATION: effusion rate for escape of a gas through a tiny hole into a vacuum
$$\propto 1/\sqrt{M}$$

KINETIC THEORY INTERPRETATION: two gases at same *T, P, V* contain equal numbers of molecules (Avogadro) so

Before effusion   During effusion

Vacuum

Porous barrier

N_2
H_2 — Lighter molecules (H_2) with higher average speeds strike the barrier more often and pass more often through it than heavier, slower molecules (N_2) at the same temperature.

$$\frac{\text{effusion rate of A}}{\text{effusion rate of B}} = \frac{u_{rms}(A)}{u_{rms}(B)} = \sqrt{\frac{M_B}{M_A}}$$

EX 12. A sample of nitrogen effuses through a tiny hole twice as fast as an unknown gas. Determine the molar mass of the unknown gas.

5.8 Collisions of Gaseous Molecules with a Wall

Consider N molecules enclosed in a fixed volume V at a temperature T. The fraction of molecules with x component of velocity between u_x and $u_x + \Delta u_x$ is

$$\frac{\Delta N_{u_x}}{N} = f(u_x)\ \Delta u_x$$

where $f(u_x)$ is the Maxwell-Boltzmann distribution law on the previous page for motion in one dimension. Then the total number of molecules with x component of velocity between u_x and $u_x + \Delta u_x$ is

$$\Delta N_{u_x} = Nf(u_x)\ \Delta u_x$$

Now examine an area A of the wall of the container and a distance $u_x \Delta t$ in front of it. A molecule with x component of velocity u_x (+ defined as going to the wall and − as going away) will strike the wall in Δt if $u_x \Delta t$ is greater than or equal to its distance from the wall. Then any molecule within the volume V' will strike the wall within Δt if its x component of velocity is greater than or equal to u_x. The fraction of molecules located within V' is just V'/V. Then the total number of molecules with velocity u_x located within V' is
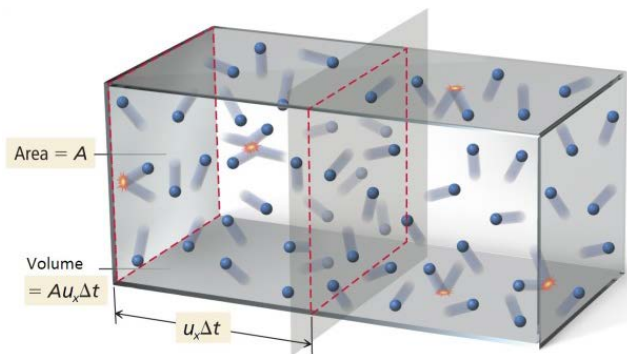
$$\Delta N_{u_x,V'} = N\frac{V'}{V} f(u_x)\ \Delta u_x$$

$$= \frac{N}{V} A\, f(u_x)\, u_x\, \Delta u_x\, \Delta t$$

and the total number colliding with the wall W in time Δt is found by summing over all u_x (actually integrating)

$$\Delta N_{\mathrm{W}} = \frac{N}{V} A\, \Delta t \int_0^\infty f(u_x)\, u_x\ du_x$$

$$= \frac{N}{V} A\, \Delta t \left(\frac{1}{2}\langle u_{1D} \rangle \right)$$

$$= \frac{N}{V} A\, \Delta t \left(\frac{1}{4}\langle u_{3D} \rangle \right)$$

The frequency of molecular collisions with the wall, Z_{W} (rate of wall collisions – note that the units are those of a frequency, s^{-1}), is

$$Z_{\mathrm{W}} = \frac{\Delta N_{\mathrm{W}}}{\Delta t}$$

$$= \frac{1}{4}\frac{N}{V} A \langle u \rangle$$

## 5.9 Collisions Between Gaseous Molecules (Intermolecular Collisions)

By rewriting the previous equation we will uncover a physical relationship common to all collisions, in particular, the rate of intermolecular collisions.

perpendicular to direction of motion

$$Z = \text{(number density)} \times \textbf{(cross sectional area)} \times \text{(relative speed)}$$

Then, Z, the number of collisions of one molecule with all of the other identical molecules per unit time is

$$Z = \frac{N}{V} \pi d^2 \sqrt{2} \langle u \rangle$$

where d is the diameter of the molecule and the factor of $\sqrt{2}$ converts the average speed to the average relative speed.

Length = u_{avg}
Volume = $\pi d^2 u_{avg}$
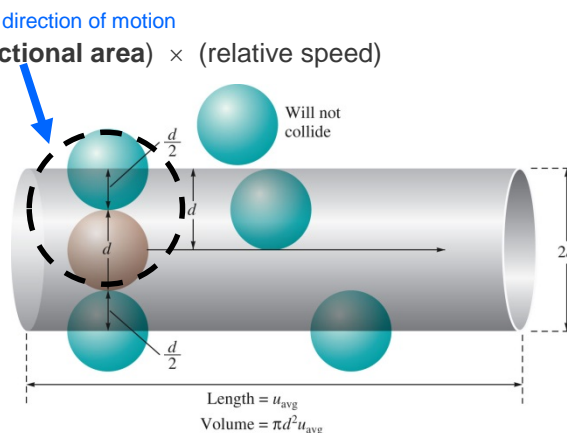
An important quantity in kinetic theory is the average distance a molecule travels between two successive intermolecular collisions. This is called the **mean free path.** The average number of collisions experienced by one molecule in unit time is Z. The distance the molecule has traveled in this unit time is $\langle u \rangle$. Therefore, the mean free path λ is

$$\lambda = \frac{\langle u \rangle}{Z} = \frac{1}{\sqrt{2}\ (N/V)\ \pi d^2}$$

EX 13. The pressure in interplanetary space is estimated to be on the order of 10^{-24} torr. Assuming the presence of only hydrogen atoms, determine the average number of atoms per m^3, the number of collisions per atom s^{-1}, and the mean free path. Take the diameter of a hydrogen atom, d, to be 0.25 nm and the temperature to be 2.7 K.

EX 14. For $C_{24}H_{38}O_4$, (M = 390.56 g/mol) the vapor pressure is 0.010 torr at 393 K. Calculate the number of molecules that evaporate into vacuum from a 1.0 cm^2 surface of the liquid at 393 K in 1.0 s. Calculate the mass that evaporates.

5.10 Real Gases - Attractive and Repulsive Forces

"The particles of the air are in contact with each other, yet they do not fit closely in every part, but void spaces are left between them, as in the sand on the sea shore: the grains of sand must be imagined to correspond to the parti-cles of air, and the air between the grains of sand to the void spaces between the particles of air. Hence, when any force is applied to it, the air is compressed, and, contrary to its nature, falls into the vacant spaces from the pressure exerted on its particles: but when the force is withdrawn, the air returns again to its former position from the elasti-city of its particles, as is the ease with horn shavings and sponge, which, when compressed and set free again, re-turn to the same position and exhibit the same bulk."   **Hero of Alexandria, ~ AD 6**
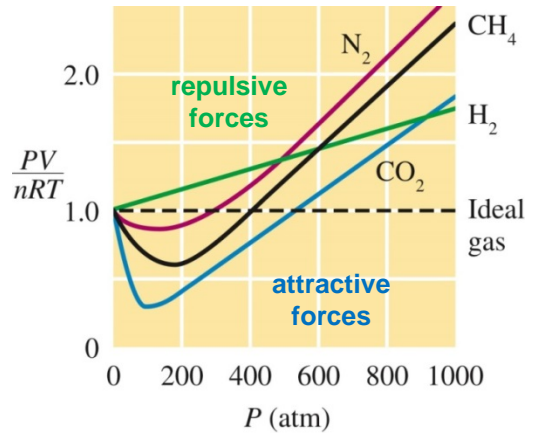

"Thus far we have always considered molecules to be material points, and thus have introduced a simplification in the model which is at once in contradiction with the actual phenomena. Even a molecule in the simplest form, consisting of a single atom, must have a certain extension; the various forces exerted upon it by the other molecules can thus not be considered to act upon a single point."
Johannes Diderik van der Waals, 1873
(Nobel Prize in Physics in 1910 "for his work on the equation of state for gases and liquids".)
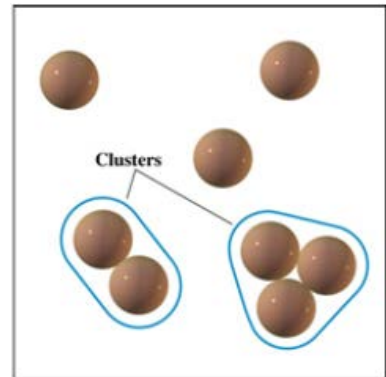
Equation of state

$$PV / nRT = 1$$

for an ideal gas. Deviations from unity due to attractive and repulsive forces between molecules. Real gases interact and have molecular volume. When molecules are very close they repel as the non-zero volumes overlap. Further separation leads to a normally weak attraction due to van der Waals forces. If the separation is very large the molecular size becomes negligible and ideal behavior is approached.

FIG IX. *PV/nRT* versus *P* for several real gases at 25°C

FIG X. Repulsive forces
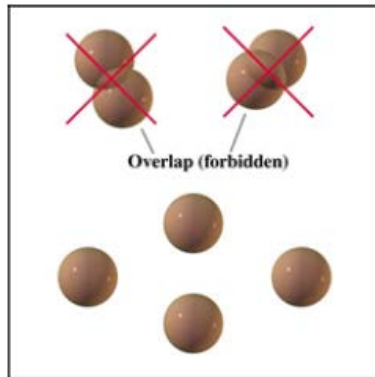
Pressure is lowered at attracttive distances and raised at very short repulsive distances result: low *T*, high *P*, get high density → gives a minimum *V* for a liquid or solid phase (liquids and solids could not exist were it not for attractive forces)

FIG XI. Attractive forces

van der Waals equation of state – model for attractive, repulsive forces

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

rearranging:

$$\frac{PV}{nRT} = \frac{1}{1 - \mathbf{b}n/V} - \frac{\mathbf{a}n}{RTV}$$

attractive forces (through **a**) – decrease ratio < 1
repulsive forces (through **b**) – increase ratio > 1

EX 15. A 1.98-L vessel contains 215 g of dry ice. After standing at 26°C, the $CO_2(s)$ turns to $CO_2(g)$. The measured pressure is 44.8 atm.
a) What pressure would an ideal gas have?

b) What pressure would a van der Waals gas have?

Van der Waals Constants of Several Gases

| Name	Formula	a (atm L^2 mol^{-2})	b (L mol^{-1})
Ammonia	NH_3	4.170	0.03707
Argon	Ar	1.345	0.03219
Carbon dioxide	CO_2	3.592	0.04267
Hydrogen	H_2	0.2444	0.02661
Hydrogen chloride	HCl	3.667	0.04081
Methane	CH_4	2.253	0.04278
Nitrogen	N_2	1.390	0.03913
Nitrogen dioxide	NO_2	5.284	0.04424
Oxygen	O_2	1.360	0.03183
Sulfur dioxide	SO_2	6.714	0.05636
Water	H_2O	5.464	0.03049
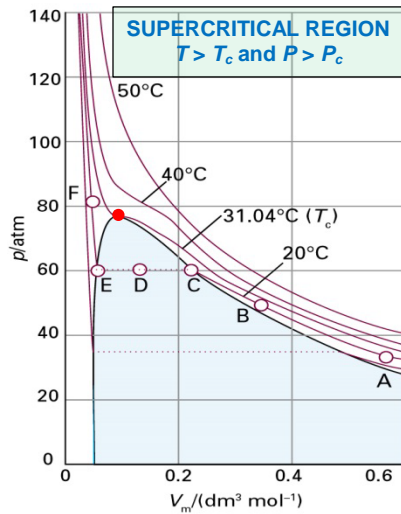
Experimental isotherms of CO_2 at several T. At large V_m, high T isotherms do not differ greatly from an ideal gas. Consider compressing gas at A at constant T. Near A, P rises in agree-ment with Boyle's law. Deviations appear at B. At C all similarity to ideal behavior lost, suddenly V_m decreases with-out a rise in P: line CDE. To the left of C liquid appears, there are two phases separated by a sharply defined surface. As V decreased from C to E, amount of liquid increases. No resistance to compression, gas responds by condensing. P corresponding to line CDE, when both liquid and vapor are in equilibrium, is the **vapor pressure** of liquid at given T. At E, sample entirely liquid. Any further reduction of V requires considerable P, as shown by sharply rising line to the left of E. "Critical isotherm", the isotherm at the critical temperature, is at 31.04°C. The critical point is marked with a bright **red** dot.
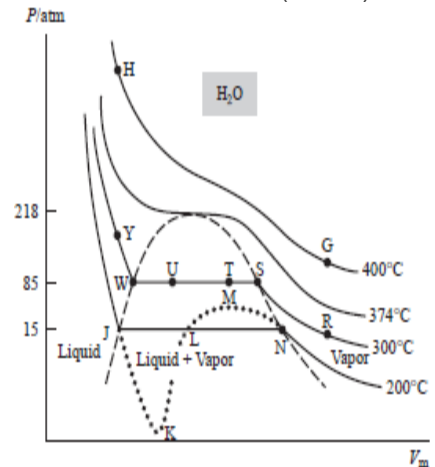
Real Gases - Condense to Liquids
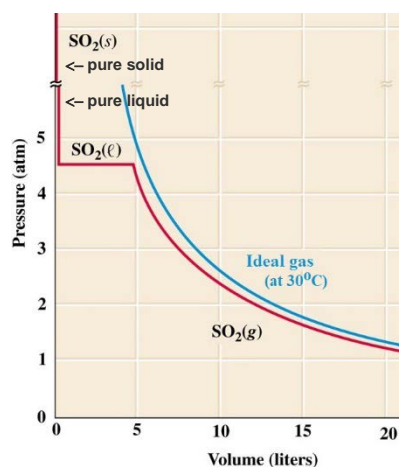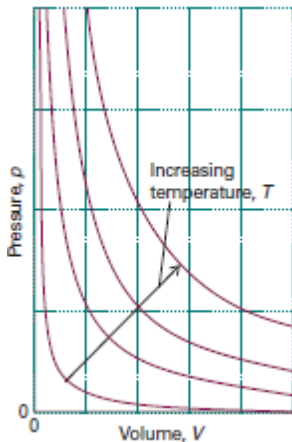
van der Waals predicts condensation, a phase transition