Gases

Z Ch 5

"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 particles 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contrary to its nature, falls into the vacant spaces from the pressure exerted on its particles: but when the force is withdrawn, the air returns again to its former position from the elasticity of its particles, as is the ease with horn shavings and sponge, which, when compressed and set free again, return to the same position and exhibit the same bulk." **Hero of Alexandria, ~ AD 60**

5.6 Kinetic Molecular Theory of Gases
5.7 Effusion and Diffusion
5.8 Collisions of Gas Particles with Container Walls
5.9 Intermolecular Collisions
5.10 Real Gases

FRIDAY
quiz

late lab reports

Q4 Ave = 7.8

REVIEW FROM MONDAY

Density and Molar Mass

definitions: density $d = m / V$, molar mass $M = m / n$

$$PV = nRT \Rightarrow n / V = P / RT$$

$$d = m / V = (n / V) M = M P / RT \Rightarrow M = dRT / P$$

EX 5. Composition of liquid is 25.23% S, 74.77% F. It boils at 29°C where density of vapor is 9.95 g L^{-1} at 738 mm Hg. What is its molecular formula? $M_S = 32.066$, $M_F = 18.998$ g/mol

Assume 100 g mol S = 25.23 / 32.066 = 0.7868 mol F = 74.77 / 18.998 = 3.9356

mol F / mol S = 5.001 / 1

so empirical formula = SF_5 (M = 127.056)

$$M = dRT / P = (9.95)(0.0820574) (29 + 273.15) / 738/760$$

$$= 254.05 \Rightarrow \text{mol / emp} = 254.05 / 127.056 \sim 2 \Rightarrow S_2F_{10}$$

REVIEW FROM MONDAY

Gas Stoichiometry

EX 7. Calcium hydride (M_{CaH2} = 42.0938 g/mol) reacts with water to form hydrogen gas. Grams of CaH_2 needed to generate 64.5 L of H_2 gas if pressure of H_2 is 814 torr at 32°C?

$$CaH_2(s) \quad + \quad 2\,H_2O(l) \quad \rightarrow \quad Ca(OH)_2(aq) \quad + \quad 2\,H_2(g)$$

x g

64.5 L
814 torr
32^oC

$$n_{CaH2} \;=\; \tfrac{1}{2}\,n_{H2} \qquad (\,PV = nRT\,) \;\; => \;\; = \; \tfrac{1}{2}\,(\,PV\,/\,RT\,)_{H2}$$

$$m \;=\; nM \;=\; MPV\,/\,2RT$$

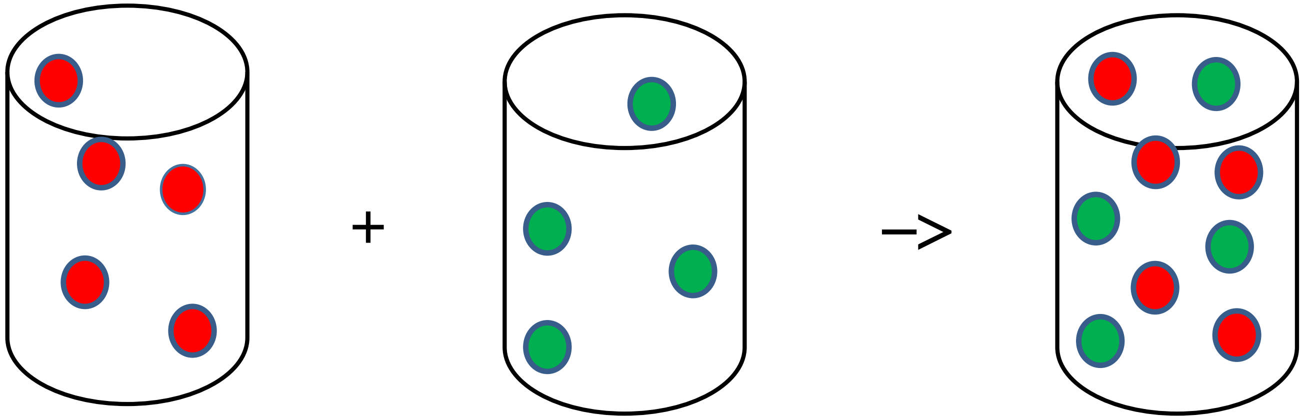
$$M \;=\; dRT\,/\,P$$

$$= (\,42.0938\,)(\,814/760\,)(\,64.15\,)\,/\,2(\,0.0820574)(\,32 + 273.15\,)$$

= **58.1 g**

REVIEW FROM MONDAY

Dalton’s Law of Partial Pressures



at same V, T

$$P = nRT / V \qquad P = nRT / V$$

$$\begin{aligned} P_{TOT} &= P + P \\ &= (n + n)\, RT / V \\ &= n_{TOT}\, RT / V \end{aligned}$$

gases act independently

$$P / P_{TOT} = n / n_{TOT} = \underset{\text{mole fraction}}{X} \Rightarrow P = X\, P_{TOT}$$

REVIEW FROM MONDAY

Collecting Gas Over Water

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? M_{NaN3} = 65.011 g/mol

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

15.00 g 745 mm (wet), 25^oC

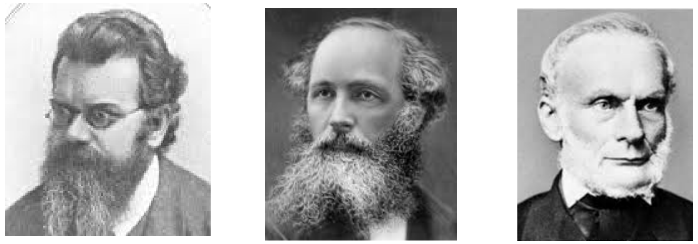
$P_{TOT} = P_{N2} + P_{H2O}$ (Dalton's Law) P_{N2}(dry) = 745 -24 = 721 mm

$n_{N2} = 3/2\ n_{NaN3} = 3/2\ 15.00/65.011 = 0.3460$

$PV = nRT$ =>

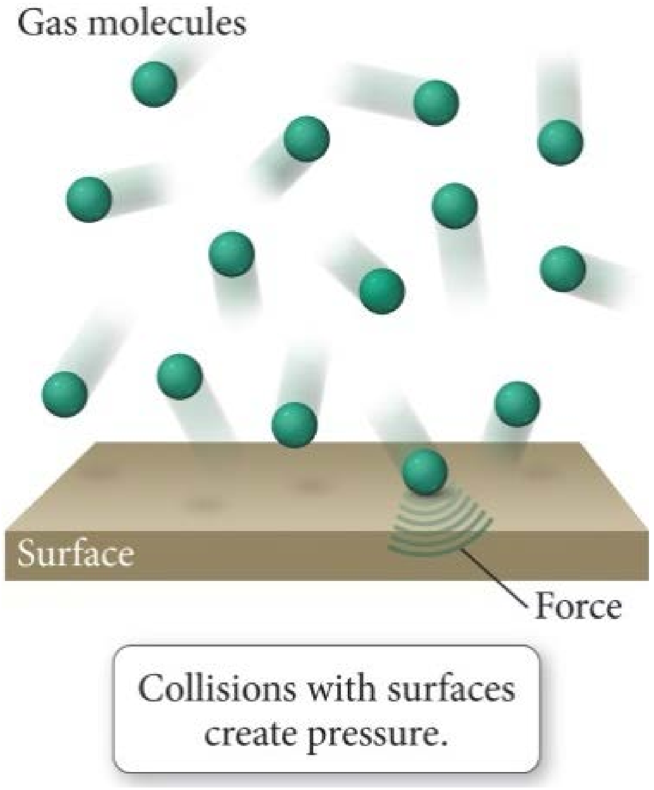
$V = nRT / P$ = (0.3460)(0.082058) (25 + 273.15) / 721/760 = **8.92 L**

Kinetic Molecular Theory of Gases



postulates of kinetic theory:

- molecular volume is negligible compared to distance between molecules
- large number of molecules, ceaseless random motion
- no forces of attraction/repulsion between molecules
- all collisions are elastic (no energy lost)



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

P = force/area

force = ma

$= m\Delta u/\Delta t$

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

$P \sim$ (# collisions) × (change in momentum per collision)

Kinetic Molecular Theory of Gases

$P \sim$ (# collisions) × (change in momentum per collision)

conclusions

1. $PV = nRT = {}^{1}/_{3}\, Nm\langle u^2\rangle$
2. ${}^{1}/_{2}\, N_o\, m\langle u^2\rangle = {}^{3}/_{2}\, RT$
3. $\langle u^2\rangle = 3RT / M$

average kinetic energy (T)

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

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

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

$PV = nRT = Nk_BT$

EX 10. What is u_{rms} for helium at -73°C? $M = 4.006$ g/mol

$u_{rms} =$

$\sqrt{[\,3\,(8.314 \text{ J mol}^{-1} \text{ K}^{-1})\,(273.15 - 73) \text{ K} / 4.0026 \times 10^{-3}}$ **kg**/mol]

$= 1120 \text{ m s}^{-1}$ [**1 J** (kinetic energy ~ mu^2) = **1 kg m² s⁻²**]

LOOK AT CHANGES

$2 \times m$ =>

2 × momentum

$P \sim m$

$2 \times N / V$ =>

2 × # collisions

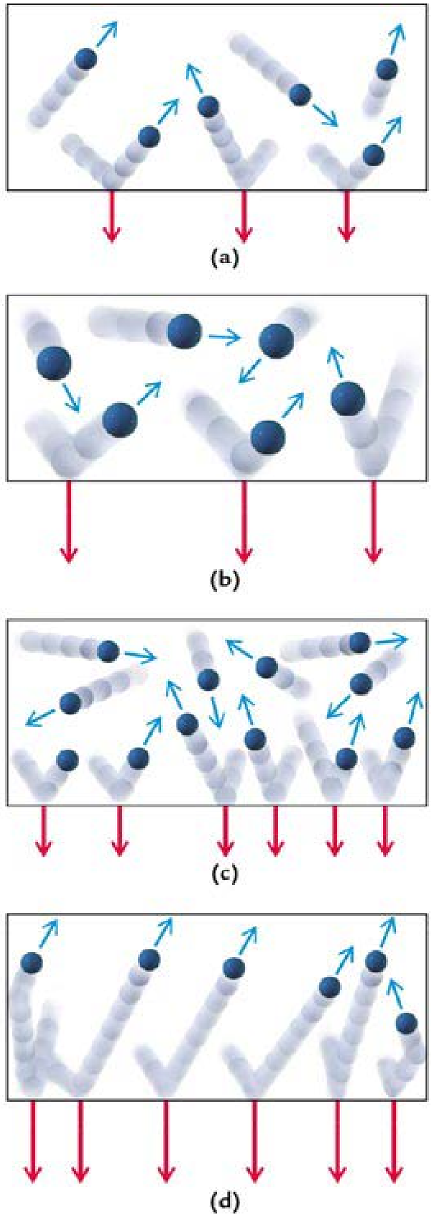
$P \sim N / V$

$2 \times u$ =>

2 × # collisions
+ 2 × momentum

$P \sim u^2$

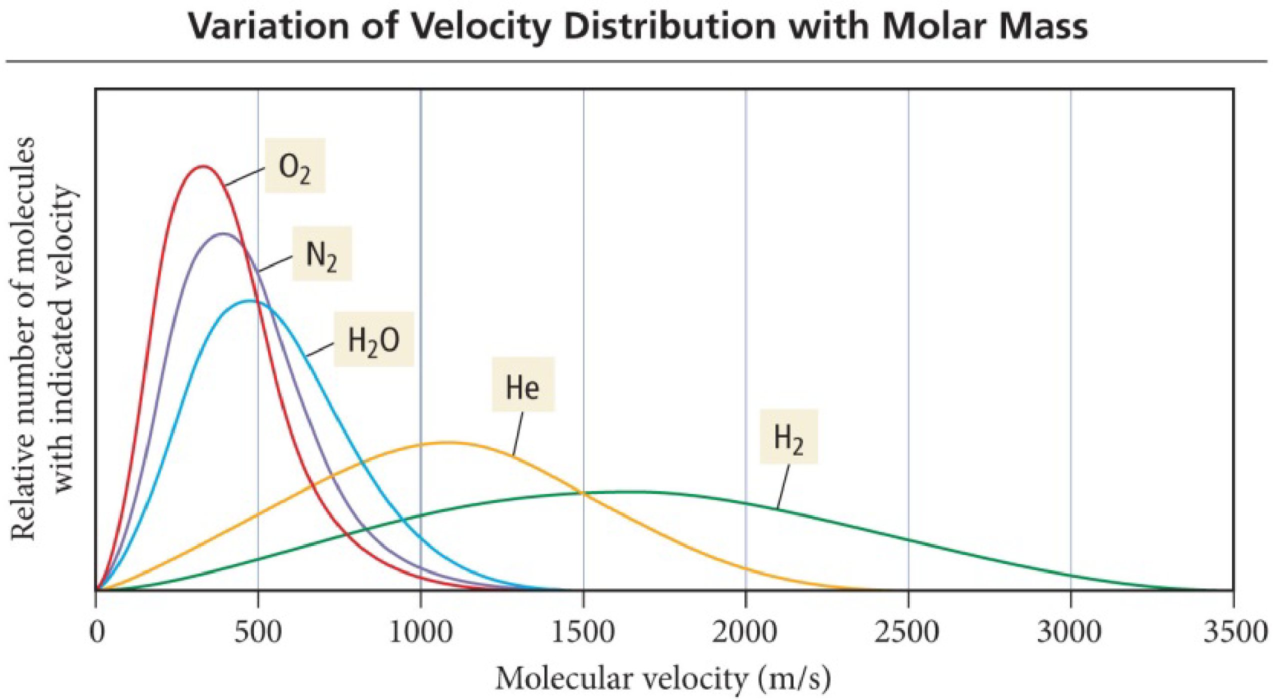
$P \sim Nmu^2 / V$



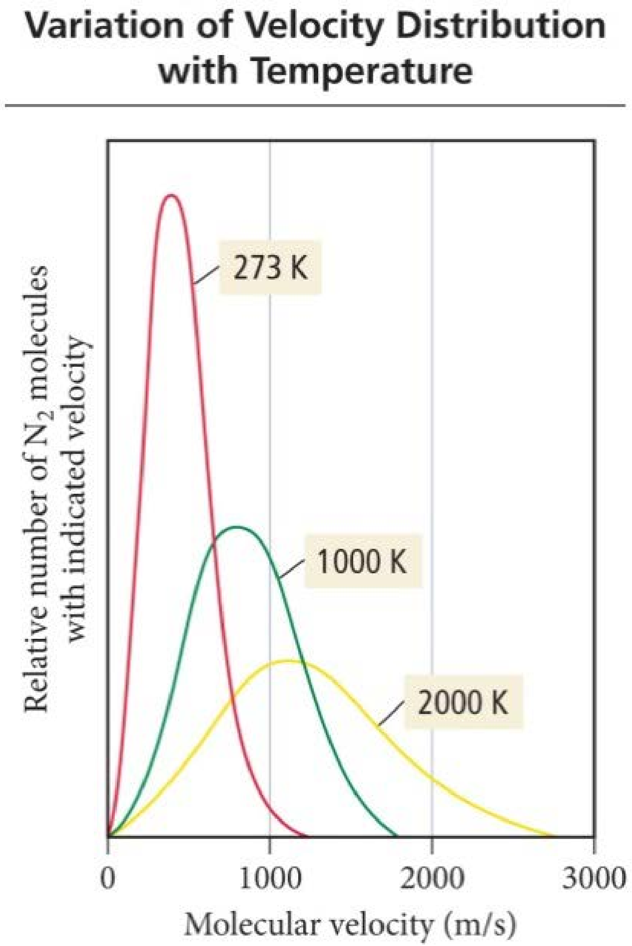
Maxwell-Boltzmann Distribution Law

distribution of velocities of the particles in an ideal gas

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



Variation of Velocity Distribution with Molar Mass



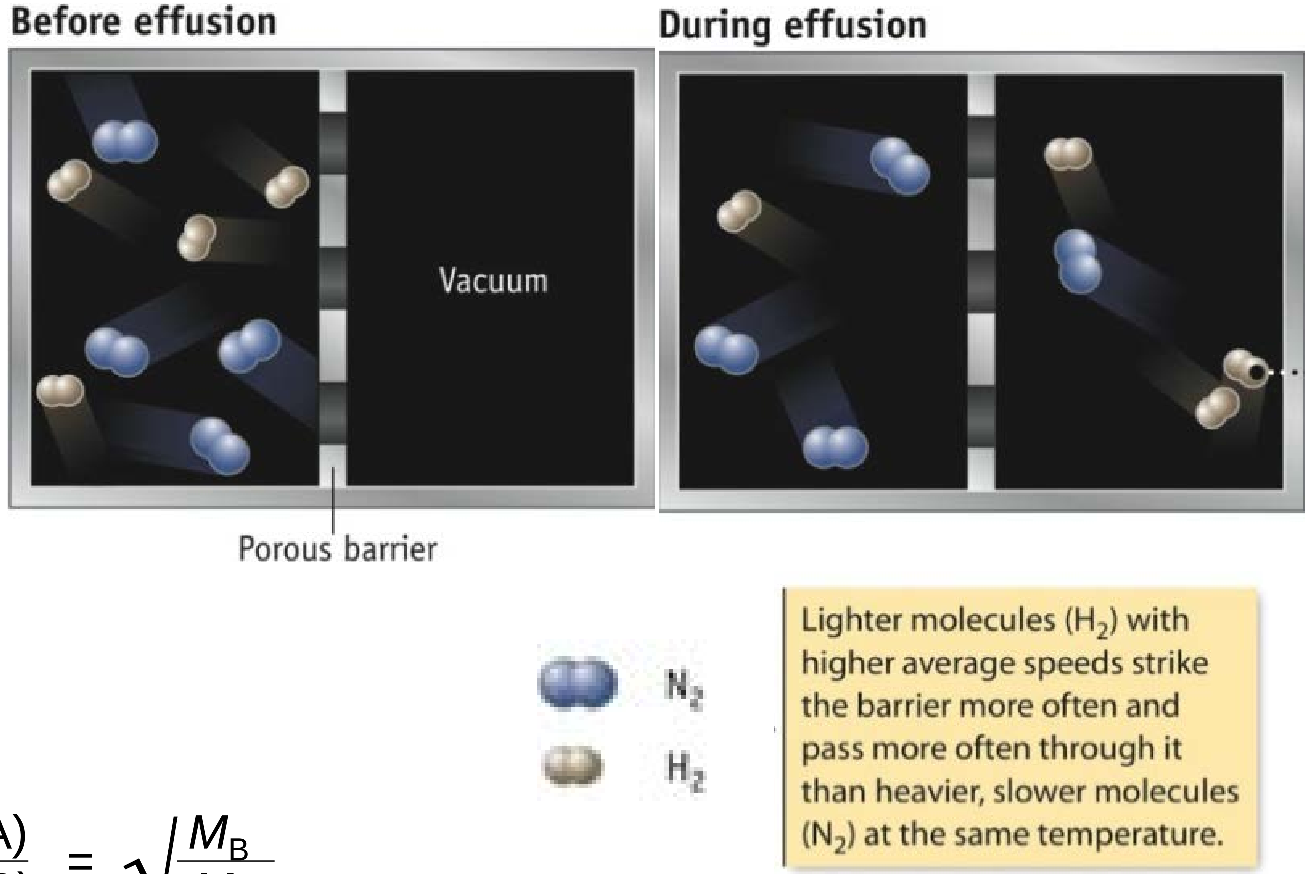
Variation of Velocity Distribution with Temperature

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



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.

$$\frac{\text{effusion rate of A}}{\text{effusion rate of B}} = \frac{\text{urms(A)}}{\text{urms(B)}} = \sqrt{\frac{M_\text{B}}{M_\text{A}}}$$

Graham’s Law of Effusion

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.

$$r_{N2} = 2\ r_x$$

$$r_{N2} / r_x = 2 = u_{rms}\ (N_2) / u_{rms}\ (x)$$

$$= \sqrt{3RT / M_{N2}}\ / \sqrt{3RT / M_x}$$

$$= \sqrt{M_x / M_{N2}}$$

$$M_x = 4\ M_{N2} = 4\ (2)\ (14.007) = 112 \text{ g/mol}$$