Chapter 11
Gases

11.1 Properties of Gases

- The properties of a gas are almost independent of its identity.

  (Gas molecules behave as if no other molecules are present.)
  - Compressible
  - Low Density
  - Expand to fill a container
  - Form homogeneous mixtures

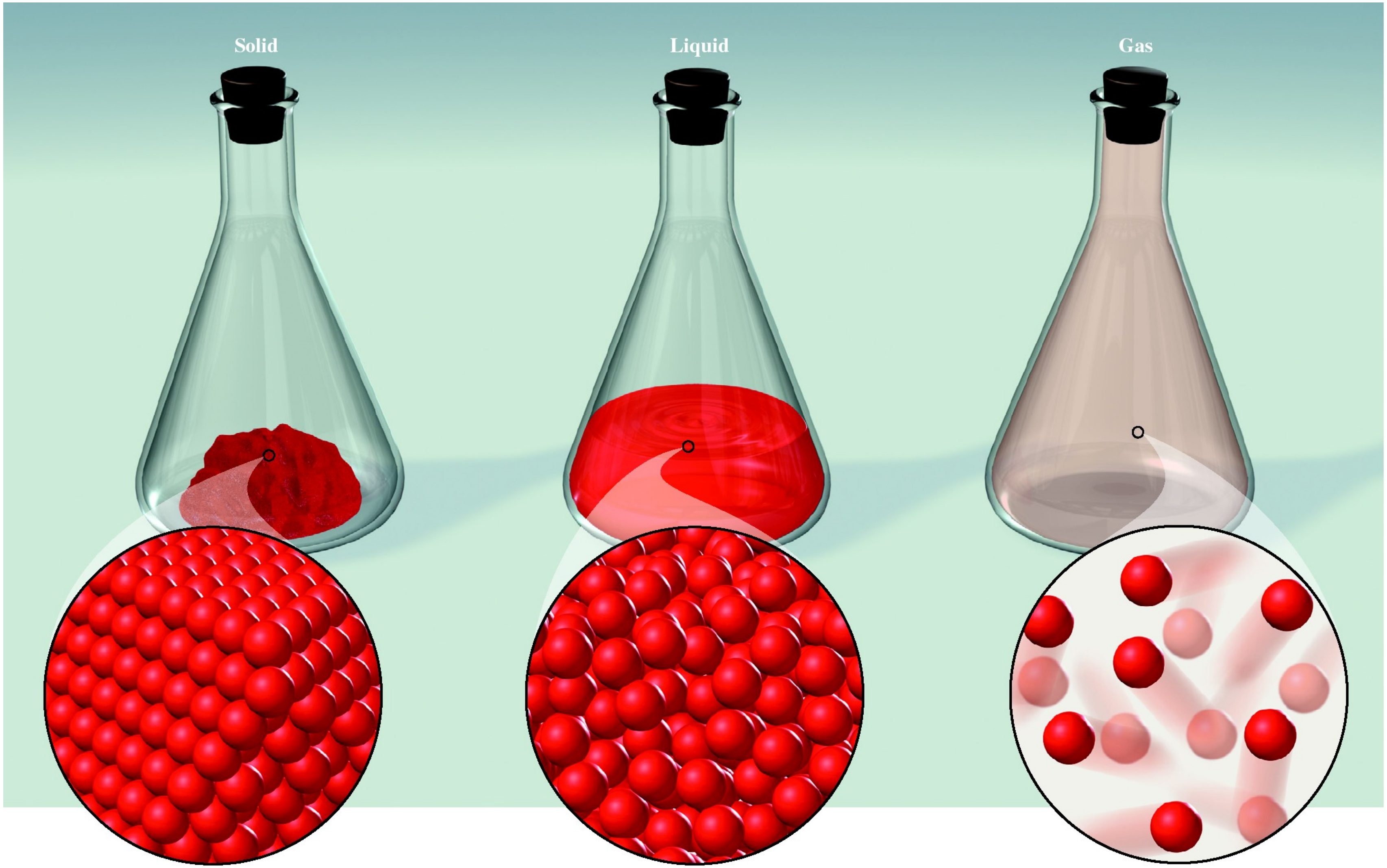
Example: Comparison of liquid and gaseous water

1 mole of water ~18 grams

One mole *liquid* water occupies less than half the volume of a golf ball.

One mole of water *vapor* (20ºC, 1 atm) occupies more than the volume of 3 basketballs.

Comparison of the Three States of Matter



- ***Pressure***: force per unit area

$$\text{pressure} = \frac{\text{force}}{\text{area}}$$

  - ***newton*** (*N*): Unit of force

$$1 \text{ N} = 1 \text{ kg} \cdot \text{m/s}^2$$

  - ***pascal*** (Pa): Unit of pressure

$$1 \text{ Pa} = 1 \text{ N/m}^2$$

  - Standard pressure

1 atm*
101,325 Pa
760 mmHg*
760 torr*
1.01325 bar
14.7 psi
*These are exact numbers.

TABLE 11.2 Units of Pressure Commonly Used in Chemistry

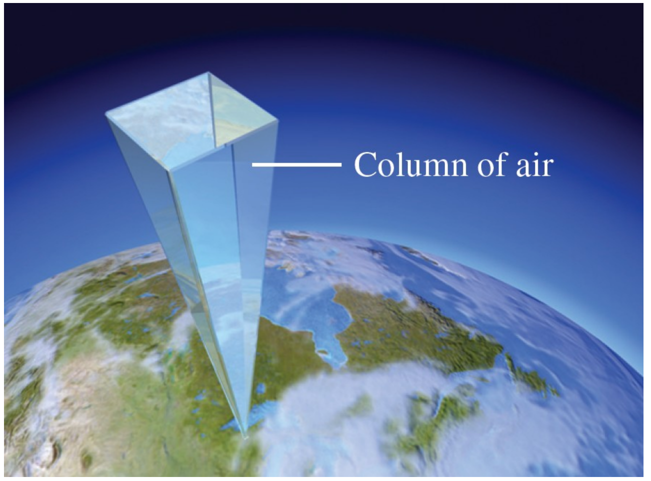
Unit	Origin	Definition
standard atmosphere (atm)	Pressure at sea level	1 atm = 101,325 Pa
mmHg	Barometer measurement	1 mmHg = 133.322 Pa
torr	Name given to mmHg in honor of Torricelli, the inventor of the barometer	1 torr = 133.322 Pa
bar	Same order of magnitude as atm, but a decimal multiple of Pa	1 bar = 1×10^5 Pa

If a weatherman says that atmospheric pressure is 29.12 inches of mercury, what is it in torr?

$$29.12\,\text{in}\left(\frac{2.54\ \text{cm}}{1\,\text{in}}\right)\left(\frac{10\ \text{mm}}{1\,\text{cm}}\right)\left(\frac{1\,\text{torr}}{1\,\text{mm}}\right) = 739.6\ \text{torr}$$

- Calculation of atmospheric pressure

Area
1 cm x 1 cm
or
0.0001 m^2



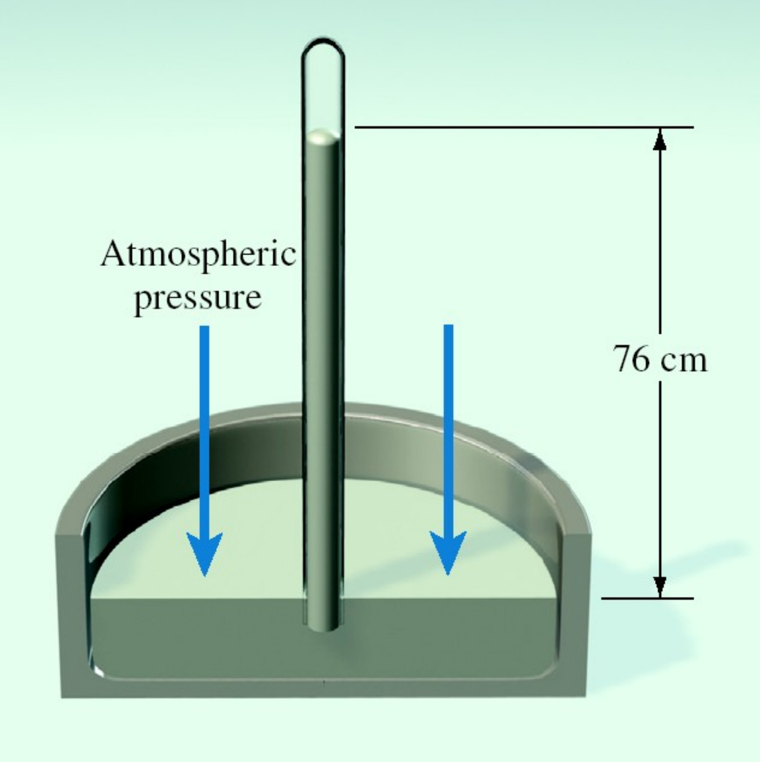
Mass: 1 kg

$$1\ \text{kg} \times \frac{9.80665\ \text{m}}{\text{s}^2} \approx 10\ \text{kg} \cdot \text{m/s}^2 = 10\ \text{N}$$

where 9.80665 m/s^2 is the gravitational constant.

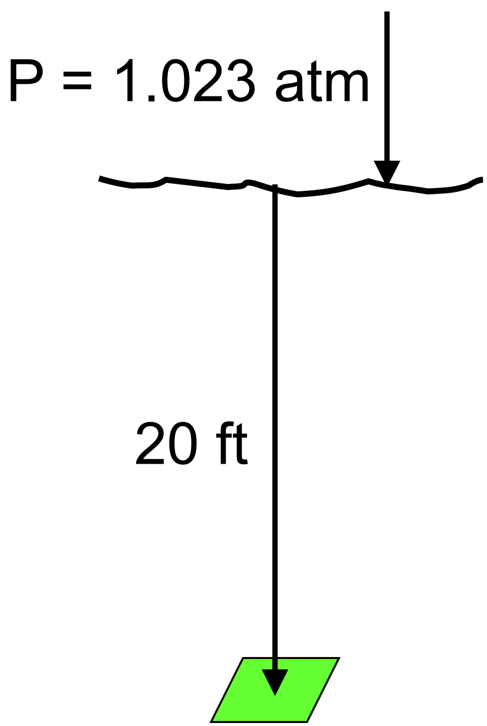
$$\frac{10\ \text{N}}{0.0001\ \text{m}^2} = 1 \times 10^5\ \text{Pa}$$

- Measurement of pressure
  - ***barometer,*** an instrument used to measure atmospheric pressure



What is the pressure (in atm) on a surface 20.0 ft under water, if the atmospheric pressure is 1.023 atm, and the densities of water and mercury are 1.00 and 13.6 g/mL, respectively?

Solution:



$$20.0\ ft \times \frac{12\ in}{1\ ft} \times \frac{25.4\ \text{mm}}{1\ \text{in}} = 6096\ mm\ H_2O$$

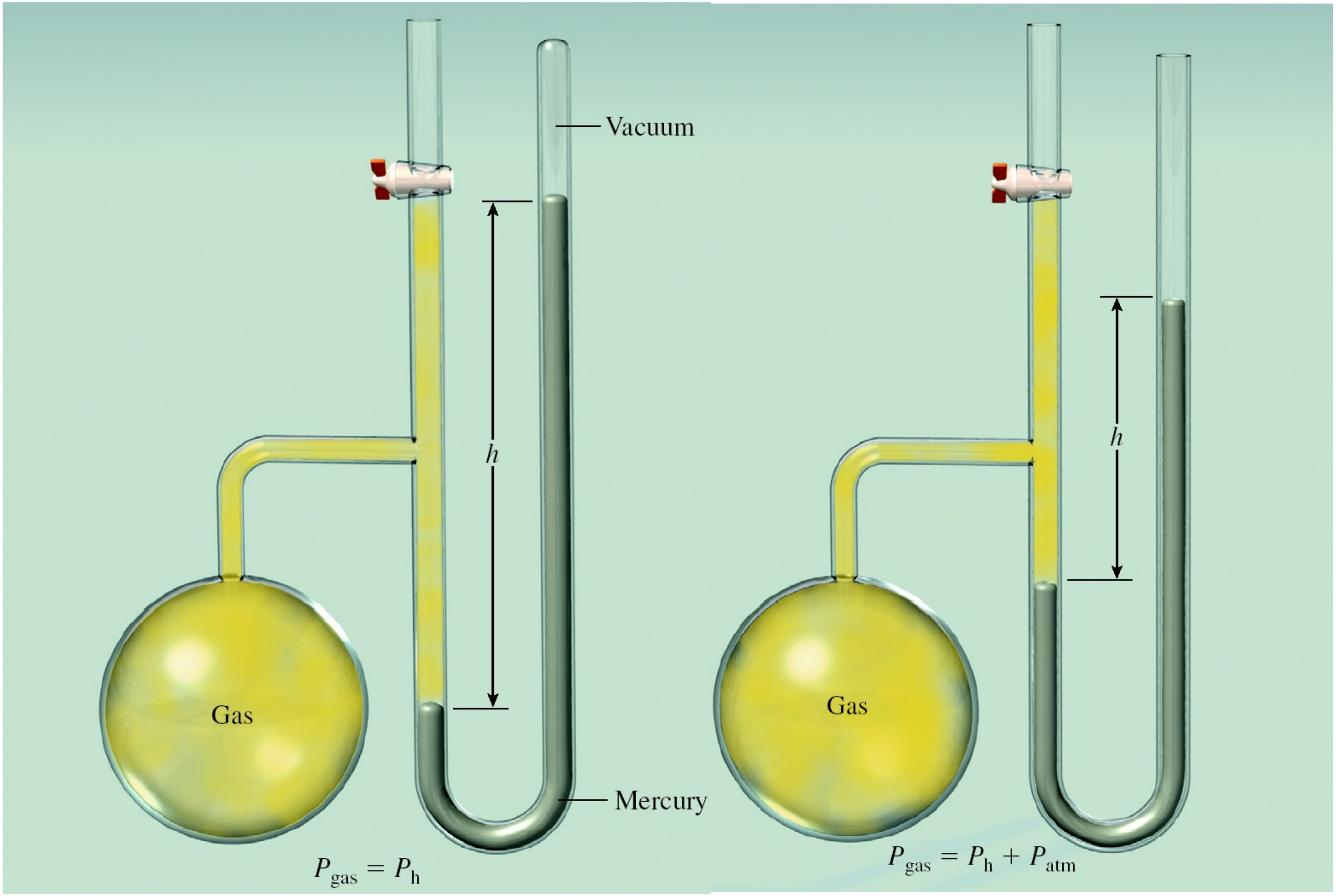
$$\times \frac{1.00\ \text{g/mL}}{13.6\ \text{g/mL}} = 448.2\ \text{mm Hg}$$

$$\times \frac{1\ \text{atm}}{760\ \text{mm Hg}} = 0.5898\ \text{atm}$$

$$\begin{array}{r} 0.5898 \\ 1.023 \\ \hline 1.613\ \text{atm} \end{array}$$

- *A* ***manometer*** is a device used to measure pressures other than atmospheric pressure.
  - Used to measure pressures of gas samples
  - Types
    - Open
    - Closed

Comparison of Open and Closed Manometers

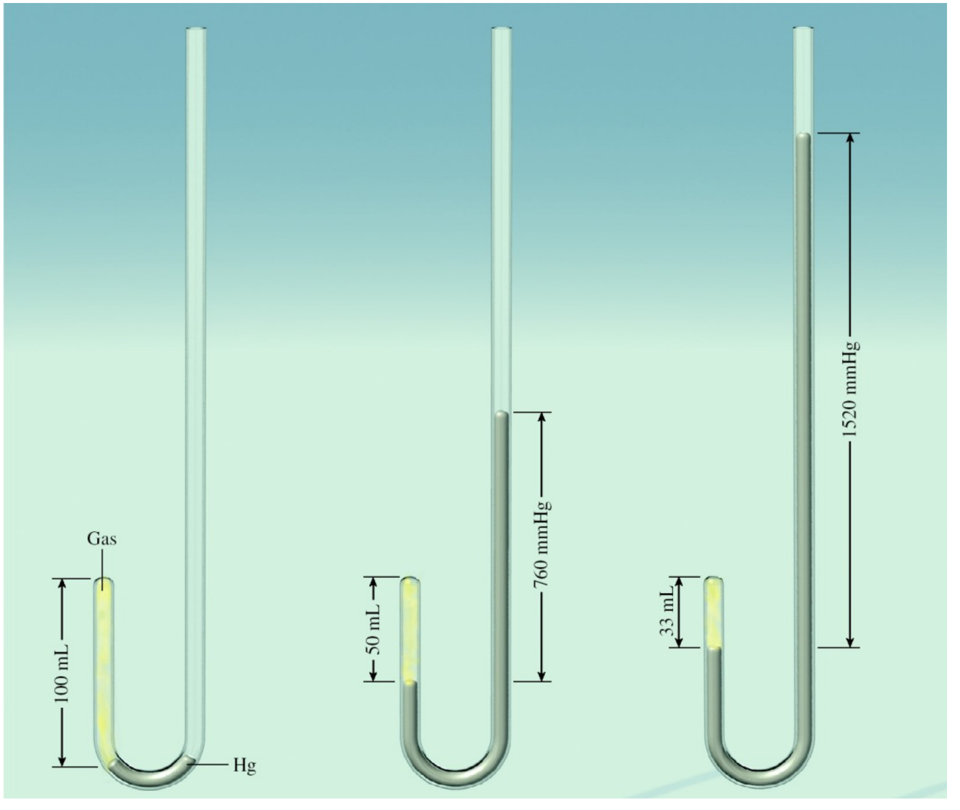


11.2 The Gas Laws

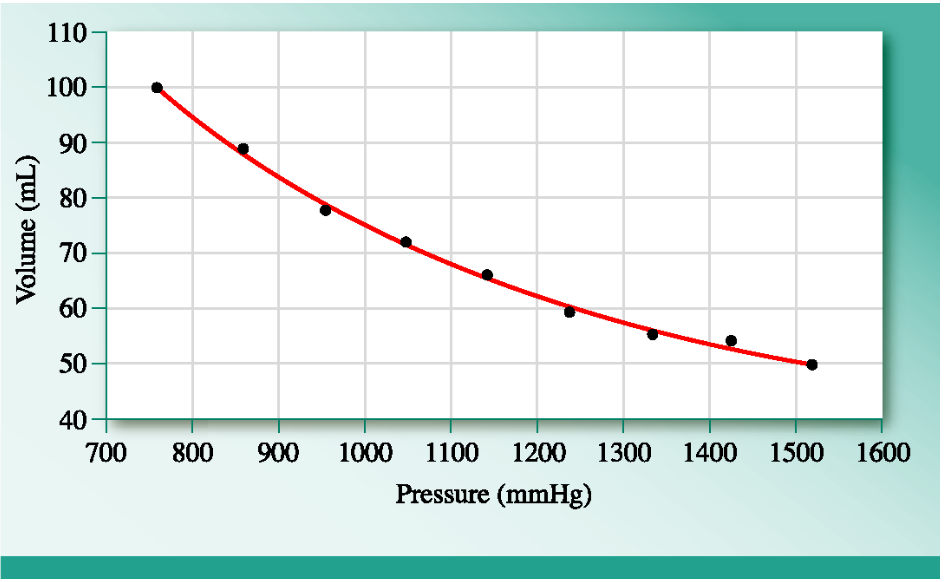
- Gas laws – empirical relationships among gas parameters
  - Volume (V)
  - Pressure (P)
  - Temperature (T)
  - Amount of a gas (n)

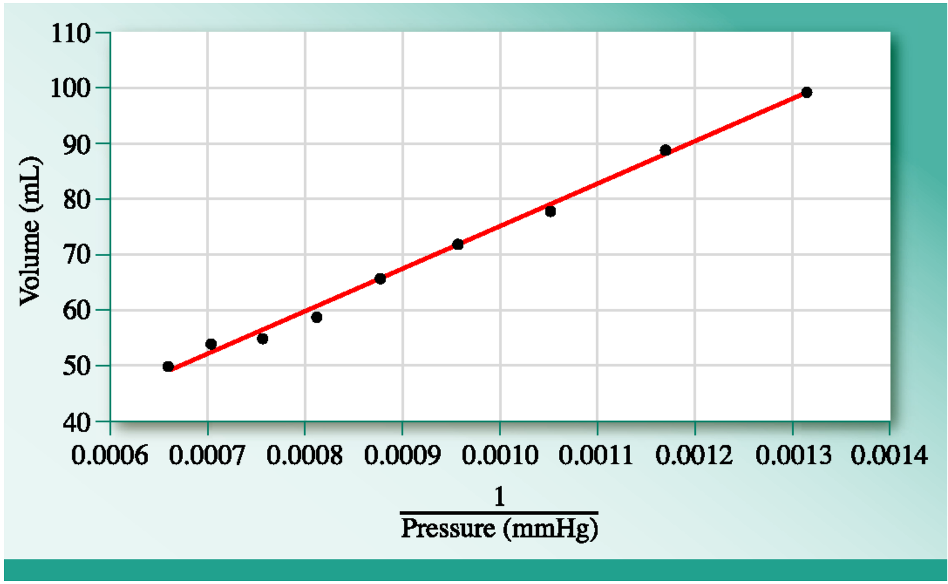
- Boyle's law: pressure-volume relationship at constant temperature

$$P_1V_1=P_2V_2$$



Graphical Expressions of Boyle's Law





Hyperbola

PV = constant

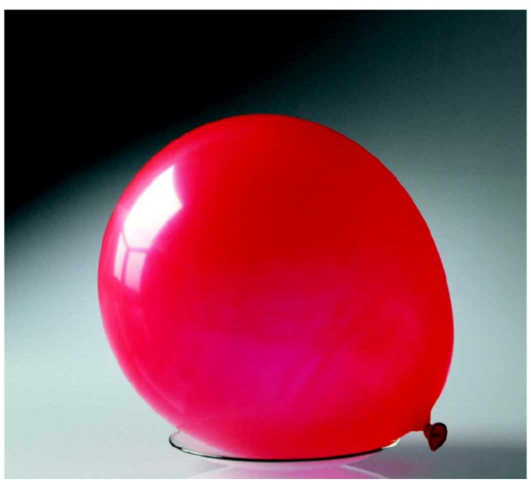
Straight Line

V = *k* / *P*

(*y* = *mx* + *b*)

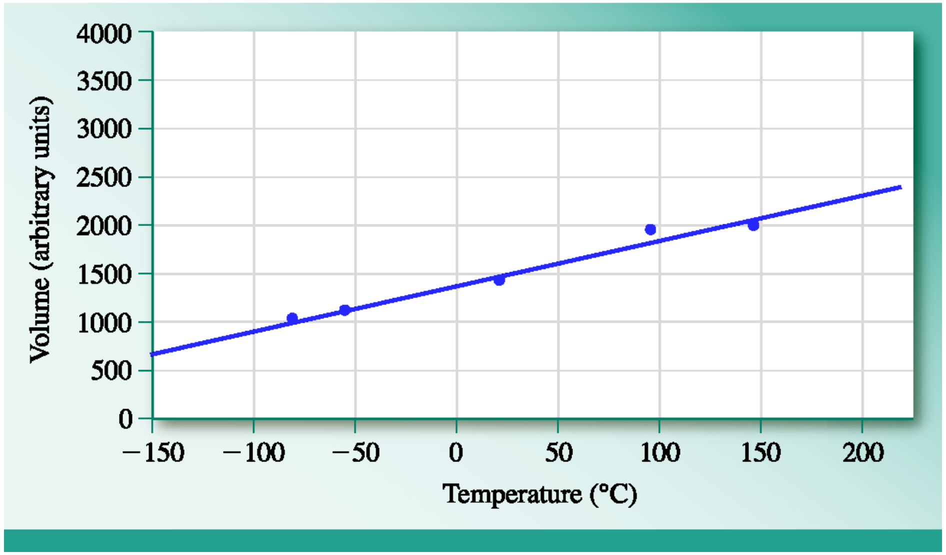
- Charles' and Guy-Lussac's law: temperature-volume relationship at constant pressure

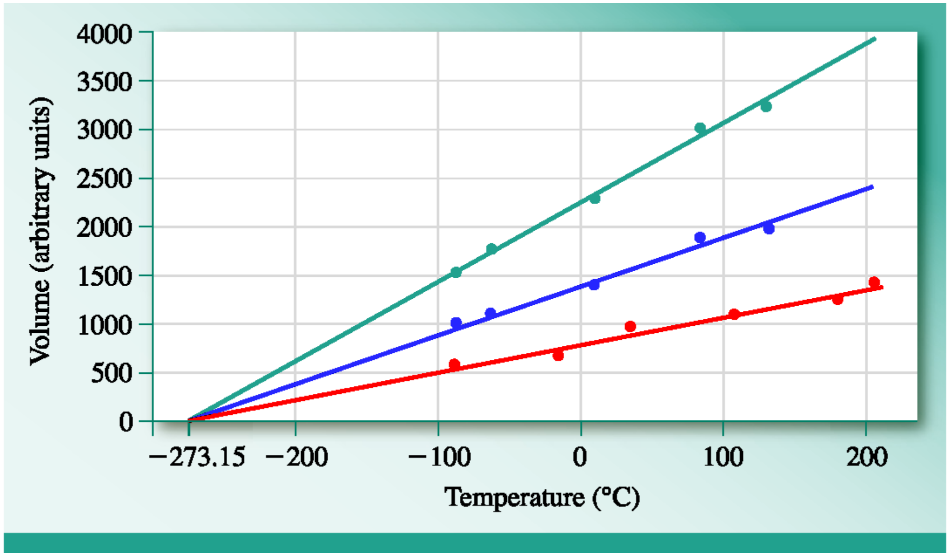
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$



Liquid N_2

Graphical Expressions of Charles' Law





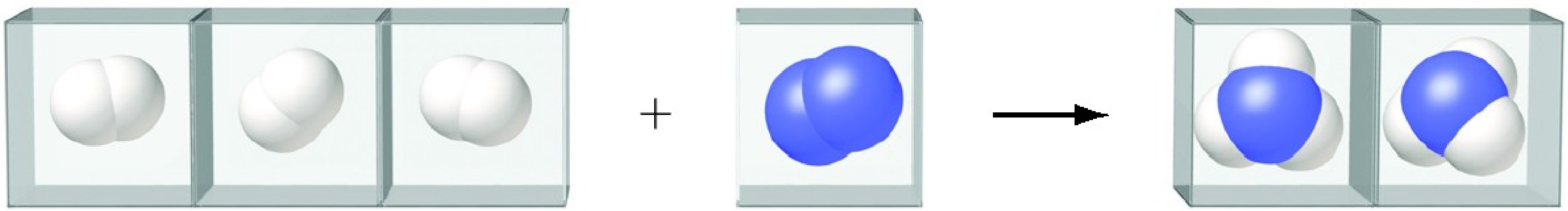
V = constant x T

Extrapolate to zero volume same T regardless of P

- Avogadro's law: the volume of a gas sample is directly proportional to the number of moles in the sample at constant pressure and temperature

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

$$3H_2(g) + N_2(g) \longrightarrow 2NH_3(g)$$



3 molecules	+	1 molecule	$\longrightarrow$	2 molecules
3 moles	+	1 mole	$\longrightarrow$	2 moles
3 volumes	+	1 volume	$\longrightarrow$	2 volumes

How will the volume of a given gas change if the quantity of gas, absolute temperature, and pressure, all double?

Avogadro $\times 2$

Charles $\times 2$

Boyle $\times 1/2$

$$2 \times 2 \times \frac{1}{2} = 2 \quad \Rightarrow \text{ volume doubles}$$

11.3 The Ideal Gas Equation

- Combining the historic gas laws yields:

Boyle's law: $V \propto \frac{1}{P}$

Charles's law: $V \propto T$

Avogadro's law: $V \propto n$

$$V \propto \frac{nT}{P}$$

- Adding the proportionality constant, *R*

$$V = R\,\frac{nT}{P}$$

$$PV = nRT$$

TABLE 11.4 Various Equivalent Expressions of the Gas Constant, R

Numerical Value	Unit
0.08206	$L \cdot atm/K \cdot mol$
62.36	$L \cdot torr/K \cdot mol$
0.08314	$L \cdot bar/K \cdot mol$
8.314	$m^3 \cdot Pa/K \cdot mol$
8.314	$J/K \cdot mol$
1.987	$cal/K \cdot mol$

Note that the product of volume and pressure gives units of *energy* (i.e., joules and calories).

- The ideal gas equation is *not* exact, but for most gases it is quite accurate near STP*
  * 760 torr (1 atm) and 273 K
- An "ideal gas" is one that "obeys" the ideal gas equation.
- At STP, 1 mol of an ideal gas occupies 22.41 L.
- Most ideal gas equation problems fall into two categories:
  - 3 of the 4 variables n, P, V & T are given.
  - Pairs of values of n, P, V or T are given.

For an ideal gas, calculate the pressure of the gas if 0.215 mol occupies 338 mL at 32.0ºC.

n = 0.215 mol

V = 338 mL = 0.338 L

T = 32.0 + 273.15 = 305.15 K

P = ?

$$PV = nRT \Rightarrow \quad P = \frac{nRT}{V}$$

$$P = \frac{(0.215\ \text{mol})\left(0.08206\ \frac{\text{L}\times\text{atm}}{\text{mol}\times\text{K}}\right)(305.15\ \text{K})}{0.338\ \text{L}} = 15.928$$

$$= 15.9\ \text{atm}$$

- Applications of the ideal gas equation
  - Relation to density (d)

$$\frac{n}{V} = \frac{P}{RT}$$

density → $$\boxed{\mathcal{M} \times \frac{n}{V}} = \frac{P}{RT} \times \mathcal{M}$$

$$d = \frac{P\mathcal{M}}{RT}$$

  - Relation to molar mass ($\mathcal{M}$)

$$\mathcal{M} = \frac{dRT}{P}$$

A steel cylinder with a volume of 68.0 L contains O_2 at a pressure of 15,900 kPa at 23ºC. What is the volume of this gas at STP?

$$P_1 = 15{,}900 \text{ kPa} \times \frac{1 \text{ atm}}{101.3 \text{ kPa}} = 157.0 \text{ atm}$$

$$P_2 = 1 \text{ atm}$$

$$T_1 = 23 + 273 = 296 \text{ K}$$

$$T_2 = 273 \text{ K}$$

$$V_1 = 68.0 \text{ L}$$

$$V_2 = ?$$

$$PV = nRT \Rightarrow nR = \frac{PV}{T} = \text{constant} = \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$V_2 = \frac{P_1V_1T_2}{T_1P_2} = \frac{(157.0 \text{ atm})(68.0 \text{ L})(273 \text{ K})}{(296 \text{ K})(1 \text{ atm})} = 9850 \text{ L}$$

11.4 Reactions with Gaseous Reactants and Products

- Amounts of gaseous reactants and products can be calculated by utilizing
  - The ideal gas law to relate moles to T, P and V.
  - Moles can be related to mass by the molar mass
  - The coefficients in the balanced equation to relate moles of reactants and products

Carbon monoxide reacts with oxygen to form carbon dioxide according to the equation:

$$2\ CO(g) + O_2(g) \longrightarrow 2\ CO_2(g)$$

What volume of O_2 is require to completely react with 65.8 mL of CO at constant temperature and pressure?

Use the fact that mL of reactant are proportional to moles of reactant.

$$65.8\ \cancel{\text{mL of CO}} \times \frac{1\ \text{mL of } O_2}{2\ \cancel{\text{mL of CO}}} =$$

- Relation of changes in pressure to moles in a reaction
  - Example
    - At constant temperature and volume

$$n = P \times \left(\frac{V}{RT}\right)$$

$$\Delta n = \Delta P \times \left(\frac{V}{RT}\right)$$

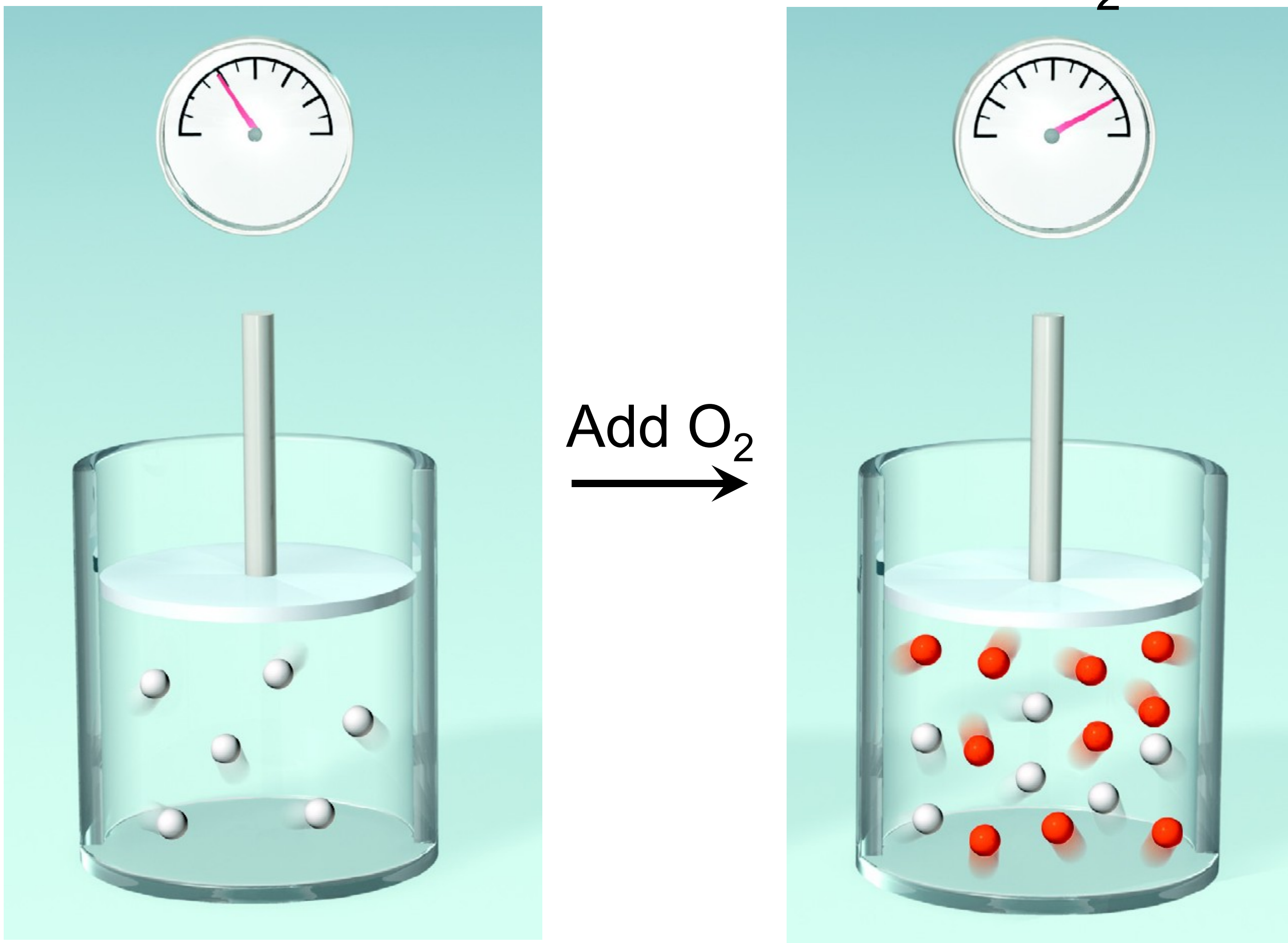
11.5 Gas Mixtures

- In gaseous mixtures, each gas behaves as though it occupies the container alone.
  - Assuming no reaction between gases
- ***partial pressure*** (P_i): the pressure exerted by each gas in a gaseous mixture
- Dalton's law of partial pressures

$$P_t = \Sigma P_i$$

Schematic of Dalton's Law

P_{N_2} $\qquad\qquad$ $P_{total} = P_{N_2} + P_{O_2}$



- ***Mole fraction*** (χ_i): the ratio of the number of moles of one component to the total number of moles in a mixture

$$\chi_i = \frac{n_i}{n_{total}}$$

  – Relation to pressure

$$\chi_i = \frac{P_i}{P_{total}}$$

$$\chi_i \times P_{total} = P_i$$

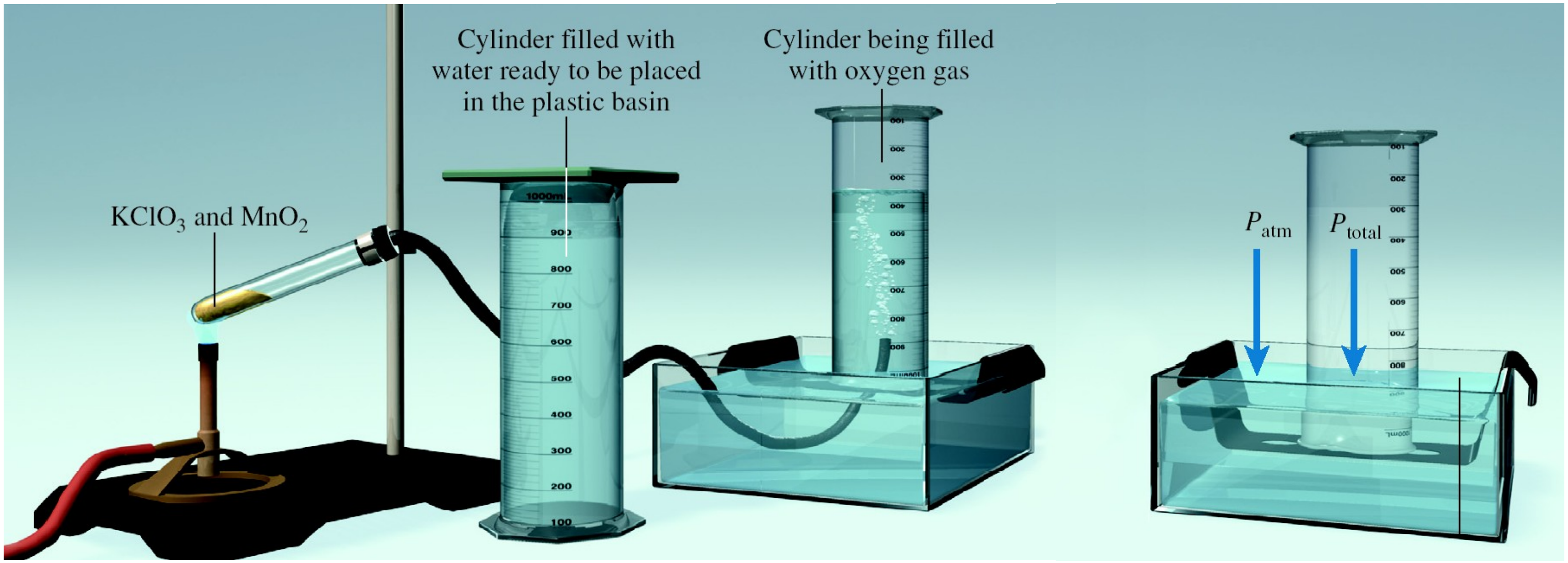
TABLE 11.5 Vapor Pressure of Water (P_{H_2O}) as a Function of Temperature

T(°C)	P (torr)	T(°C)	P (torr)	T(°C)	P (torr)
0	4.6	35	42.2	70	233.7
5	6.5	40	55.3	75	289.1
10	9.2	45	71.9	80	355.1
15	12.8	50	92.5	85	433.6
20	17.5	55	118.0	90	525.8
25	23.8	60	149.4	95	633.9
30	31.8	65	187.5	100	760.0

Oxygen was produced and collected over water at 22ºC and a pressure of 754 torr.

$$2\,KClO_3(s) \rightarrow 2\,KCl(s) + 3\,O_2(g)$$

325 mL of gas were collected and the vapor pressure of water at 22ºC is 21 torr. Calculate the number of moles of O_2 and the mass of $KClO_3$ decomposed.



$$P_{total} = P_{O_2} + P_{H_2O} = P_{O_2} + 21 \text{ torr} = 754 \text{ torr}$$

$$P_{O_2} = 754 \text{ torr} - 21 \text{ torr} = 733 \text{ torr} = 733/760 \text{ atm}$$

$$V = 325 \text{ mL} = 0.325 \text{ L}$$

$$T = 22^{\circ}\text{C} + 273 = 295 \text{ K} \qquad n = \frac{PV}{RT}$$

$$n_{O_2} = \frac{\left({}^{733}\!/\!_{760} \text{ atm}\right)(0.325 \text{ L})}{\left(0.08206 \ \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(295 \text{ K})} = 1.29\times10^{-2} \text{ mol O}_2$$

$$2\,KClO_3(s) \rightarrow 2\,KCl(s) + 3\,O_2(g)$$

$$1.29\times10^{-2} \text{ mol O}_2 \left(\frac{2 \text{ mol KClO}_3}{3 \text{ mol O}_2}\right)\left(\frac{122.6 \text{ g KClO}_3}{1 \text{ mol KClO}_3}\right) =$$

$$= 1.06 \text{ g KClO}_3$$

11.6 The Kinetic Molecular Theory

- A gas is composed of particles that are separated by relatively large distances. The volume occupied by individual molecules is negligible.
- Gas molecules are constantly in random motion, moving in straight paths, colliding with the walls of their container and with one another in perfectly elastic collisions.
- Gas particles exert no attractive or repulsive forces on one another.
- The average kinetic energy of the particles is proportional to the absolute temperature.

- Application to the gas laws
  - Gases are compressible because the gas molecules are separated by large distances.
  - The magnitude of P depends on how often and with what force the molecules strike the container walls.
  - At constant T, as V increases, each particle strikes the walls less frequently and P decreases.

(Boyle’s Law)

- To maintain constant *P*, as *V* increases *T* must increase; fewer collisions require harder collisions.

(Charles' Law)

- To maintain constant *P* and *T*, as *V* increases *n* must increase.

(Avogadros' Law)

- Gas molecules do not attract or repel one another, so one gas is unaffected by the other and the total pressure is a simple sum.

(Dalton's Law)

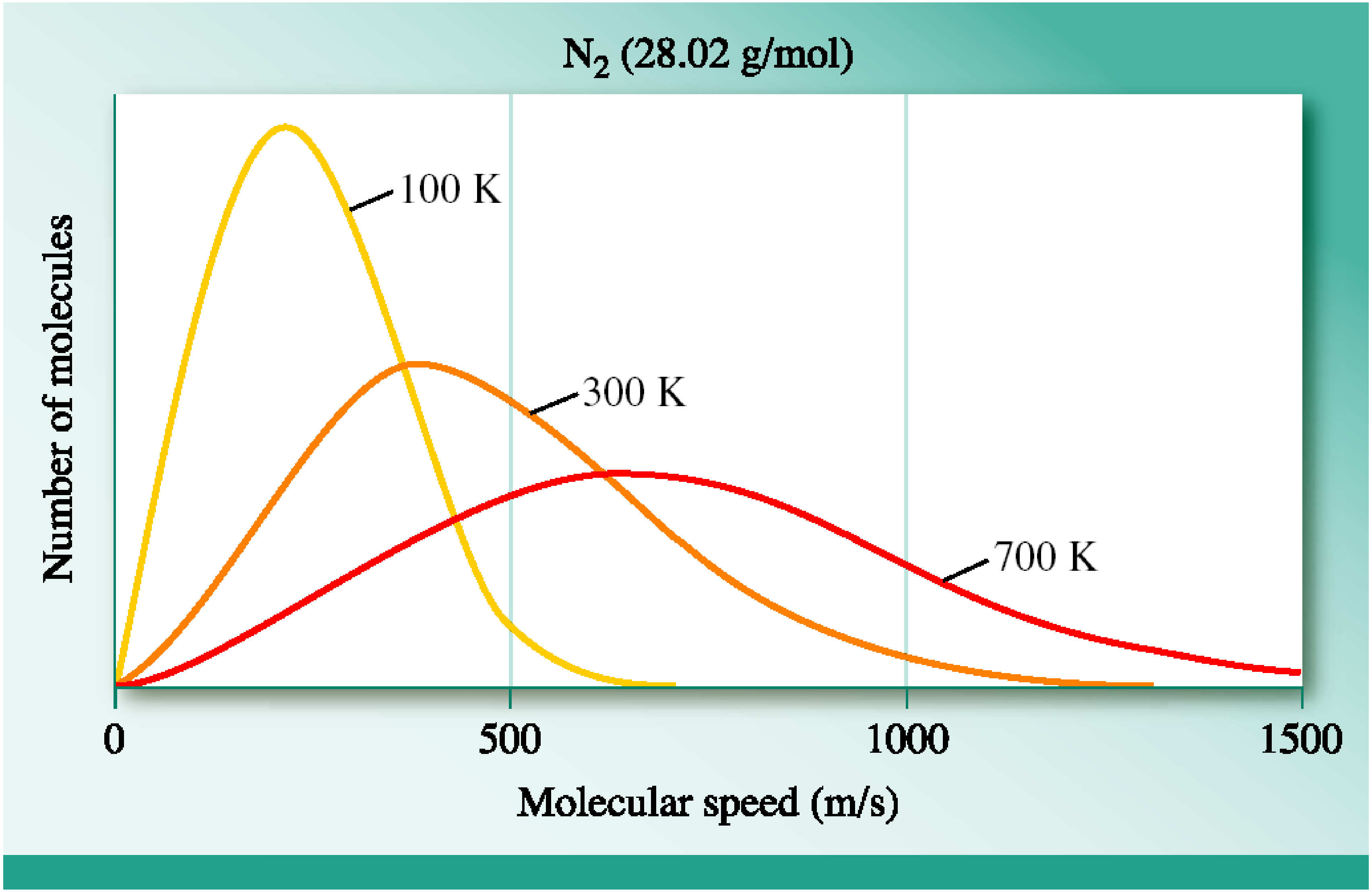
- Molecular speed
  - ***Root mean square*** (***rms***) ***speed*** (***u*****rms**)

$$u_{\text{rms}} = \sqrt{\frac{3RT}{\mathcal{M}}}$$

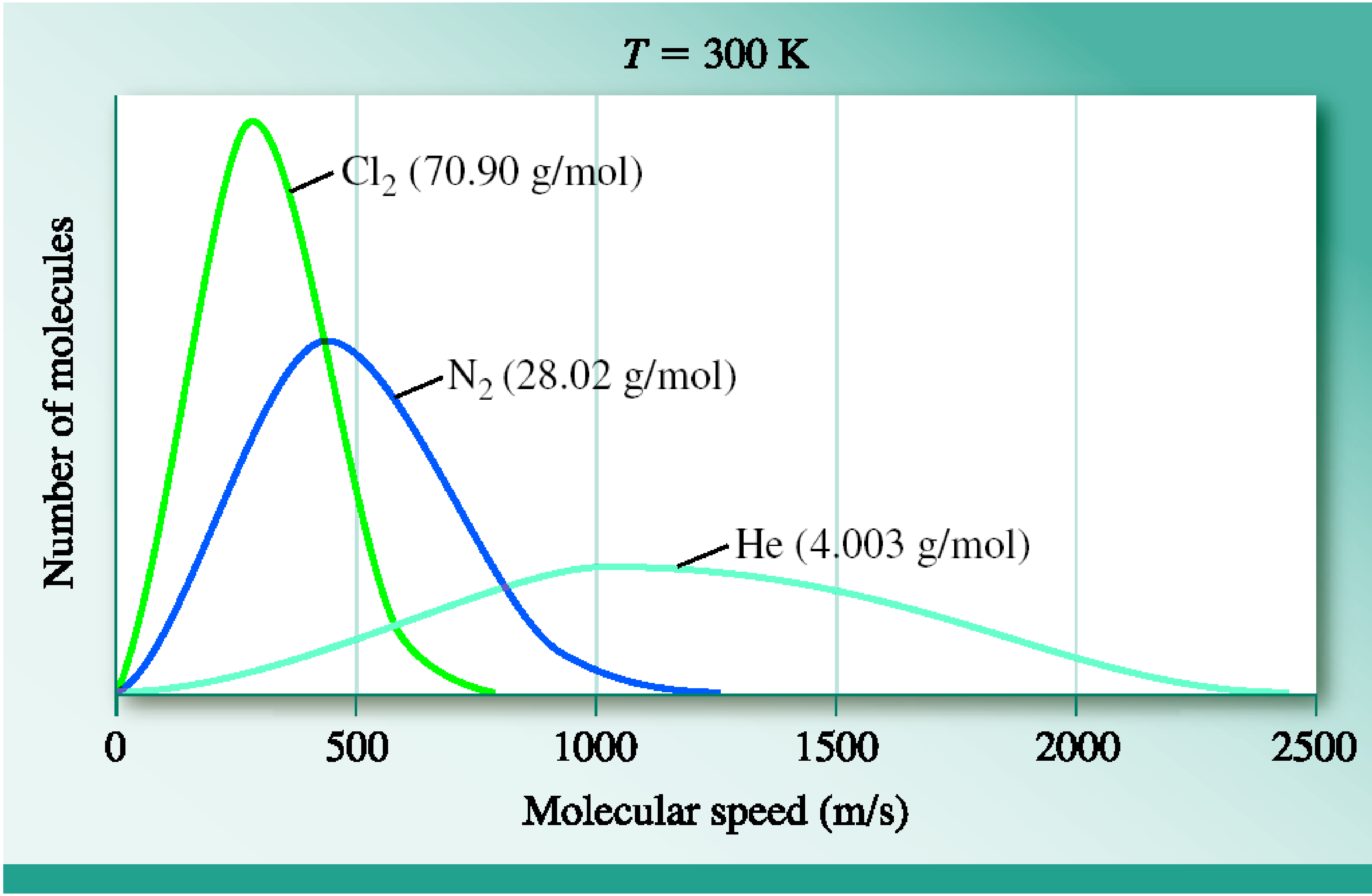
- For two gases (1 and 2)

$$\frac{u_{\text{rms}}(1)}{u_{\text{rms}}(2)} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}}$$

Effect of Temperature on Molecular Speed



Effect of Molar Mass on Molecular Speed



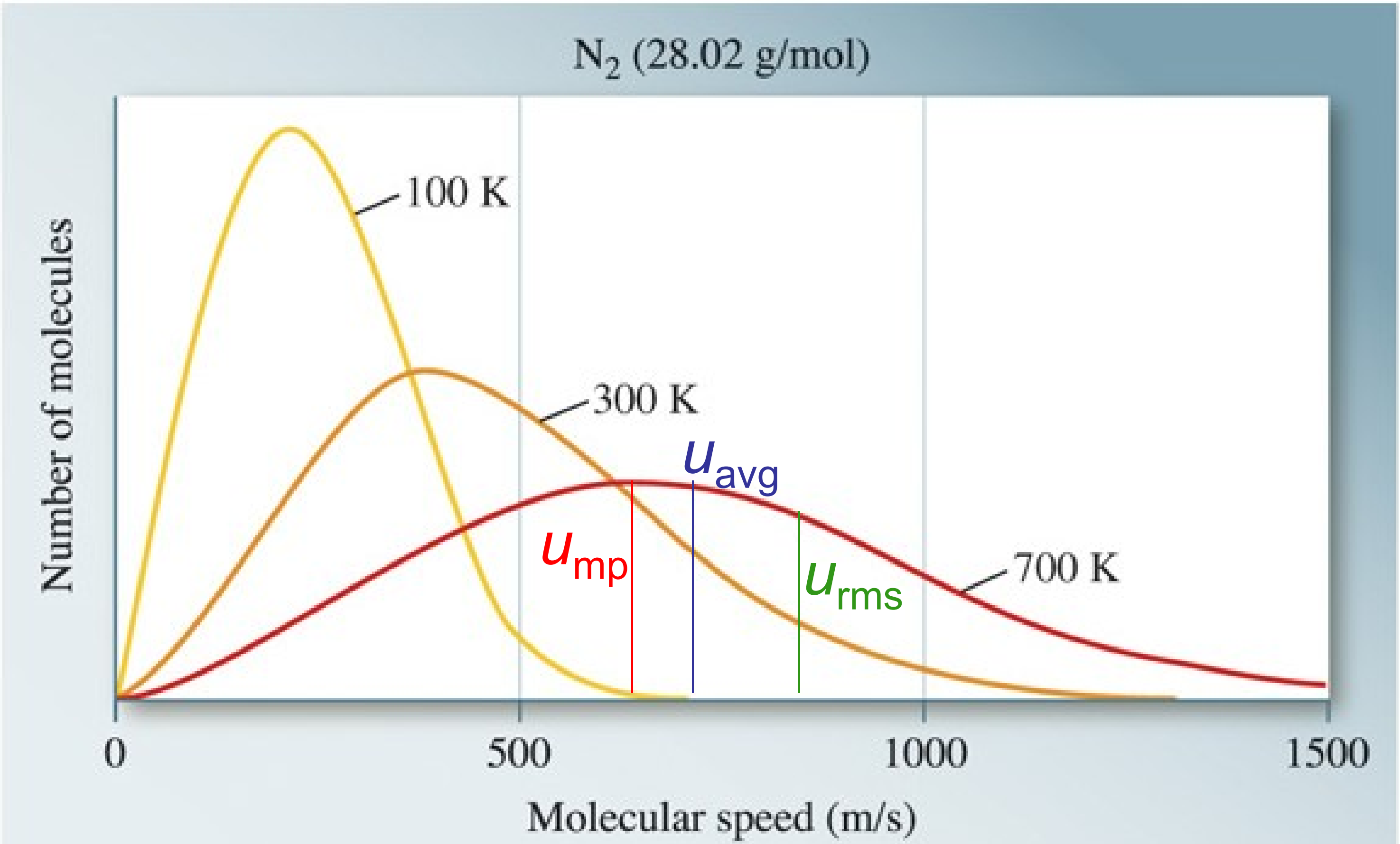
- Comparison of rms and other speed measurements
  - Mean or average speed (u_{avg})
  - Most probable speed (u_{mp})
  - Rms speed (u_{rms})

  Example: Assume five speeds: 2, 4, 4, 6 and 8 m/s

$$u_{\text{avg}} = \frac{2+4+4+6+8}{5} = \frac{24}{5} = 4.8 \text{ m/s}$$

$$u_{\text{mp}} = 4.0 \text{ m/s}$$

$$u_{\text{rms}} = \sqrt{\frac{2^2+4^2+4^2+6^2+8^2}{5}} = \sqrt{\frac{136}{5}} = 5.2 \text{ m/s}$$


N2 (28.02 g/mol)
100 K
300 K
700 K
u avg
u mp
u rms
Number of molecules
0
500
1000
1500
Molecular speed (m/s)

Place the following gases in order of increasing r.m.s. speed at 300 K,

H_2, CO_2, Ne, NH_3, Cl_2

$$u_{Cl_2} < u_{CO_2} < u_{Ne} < u_{NH_3} < u_{H_2}$$

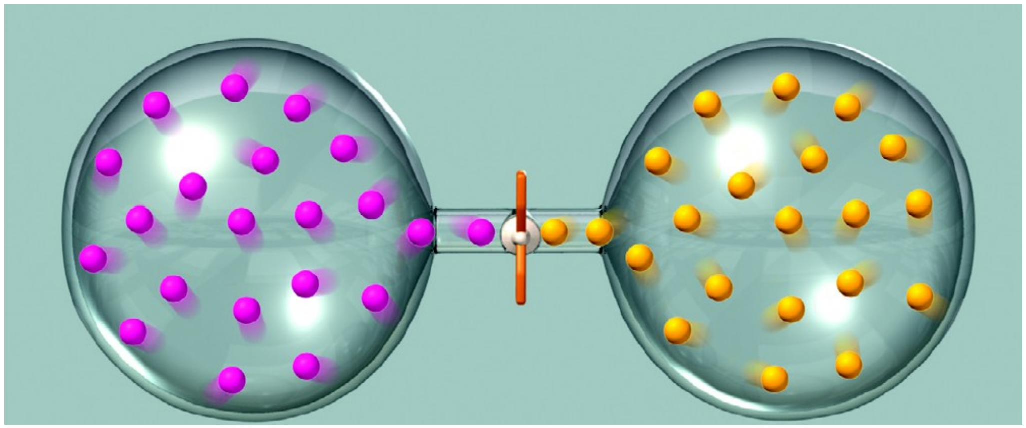
Which one has the highest average kinetic energy?

At the same temperature, all have the same average kinetic energy.

How fast do N_2 molecules move at room temperature (25^oC)?

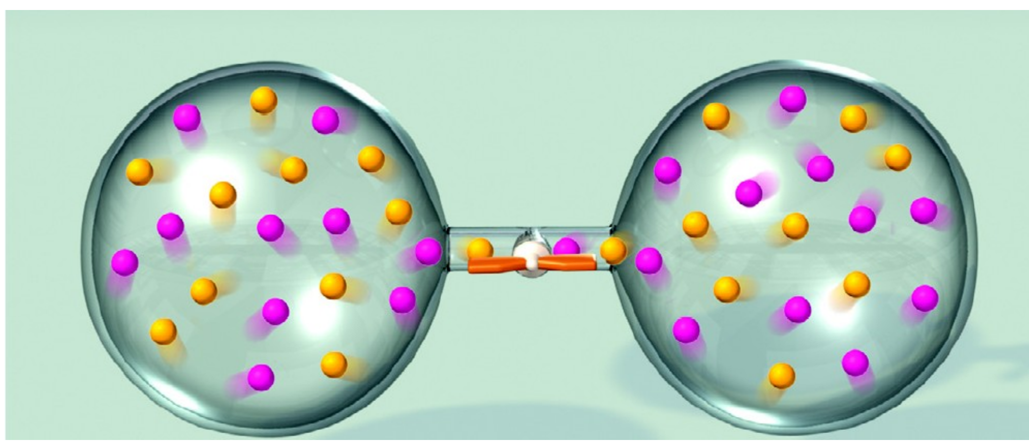
$$u = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3\left(8.314\ \frac{\text{kg}\cdot\text{m}^2}{\text{s}^2\ \text{mol K}}\right)(298\ \text{K})}{28.0\times10^{-3}\ \frac{\text{kg}}{\text{mol}}}} = 515\ \frac{\text{m}}{\text{s}} = 1150\ \text{mph}$$

- ***Diffusion***: the mixing of gases as a results of random motion and collisions.

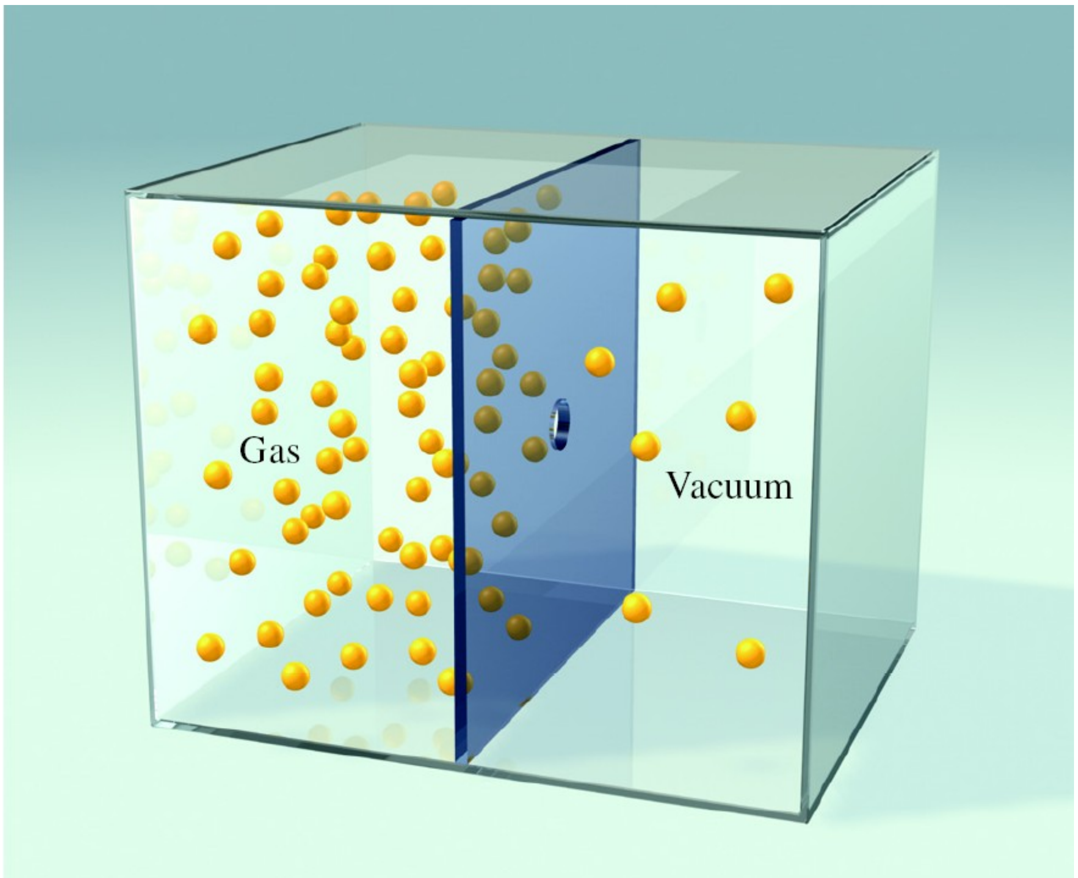


Open valve

$$\text{Rate} \propto \frac{1}{\sqrt{\mathcal{M}}}$$



- ***Effusion***: the escape of a gas from a container to a region of vacuum

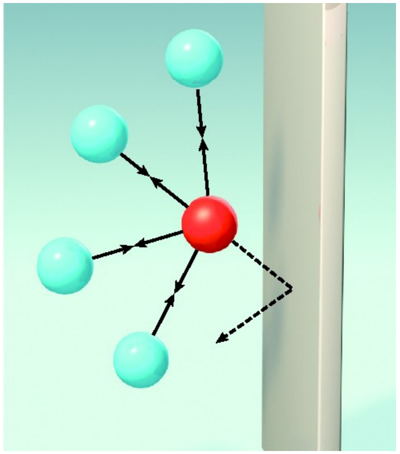


$$\text{Rate} \propto \frac{1}{\sqrt{\mathcal{M}}}$$

11.7 Deviation from Ideal Behavior

- Real gases do not always behave ideally under certain conditions due to
  - Gas molecules occupy significant volume (at high pressures)
  - Gas molecules experience intermolecular forces of attraction and repulsion (at low temperatures)

Effect of intermolecular forces on P



- Van der Waal's equation corrects for
  - Pressure deviations

$$P_{\text{ideal}} = P_{\text{real}} + \frac{an^2}{V^2}$$

where *a* is a constant

  - Volume effects

$$V_{\text{real}} = V_{\text{ideal}} - nb$$

where *b* is a constant

- The ideal gas law

$$PV = nRT$$

becomes van der Waal's equation

$$\underbrace{\left(P + \frac{an^2}{V^2}\right)}_{\text{corrected pressure term}} \underbrace{(V - nb)}_{\text{corrected volume term}} = nRT$$

a and *b* have specific values for each gas

TABLE 11.6 Van der Waals Constants of Some Common Gases

Gas	$a\left(\frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2}\right)$	$b\left(\frac{\text{L}}{\text{mol}}\right)$	Gas	$a\left(\frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2}\right)$	$b\left(\frac{\text{L}}{\text{mol}}\right)$
He	0.034	0.0237	O_2	1.36	0.0318
Ne	0.211	0.0171	Cl_2	6.49	0.0562
Ar	1.34	0.0322	CO_2	3.59	0.0427
Kr	2.32	0.0398	CH_4	2.25	0.0428
Xe	4.19	0.0510	CCl_4	20.4	0.138
H_2	0.244	0.0266	NH_3	4.17	0.0371
N_2	1.39	0.0391	H_2O	5.46	0.0305

Key Points

- Properties of gases
  - Gas pressure
    - Units
    - Calculation
    - Measurement
- The gas laws
  - Boyle's law
  - Charles' law

Key Points

  - Avogadro's law
- The ideal gas law
- Reactions with gaseous reactants and products
- Gas mixtures
  - Dalton's law
  - Mole fractions
  - Partial pressures

Key Points

- The kinetic molecular theory
  - Assumptions
  - Application to the gas laws
  - Molecular speed
  - Diffusion and effusion
- Deviation from ideal behavior
  - Factors causing deviation
  - Van der Waal’s equation