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

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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.

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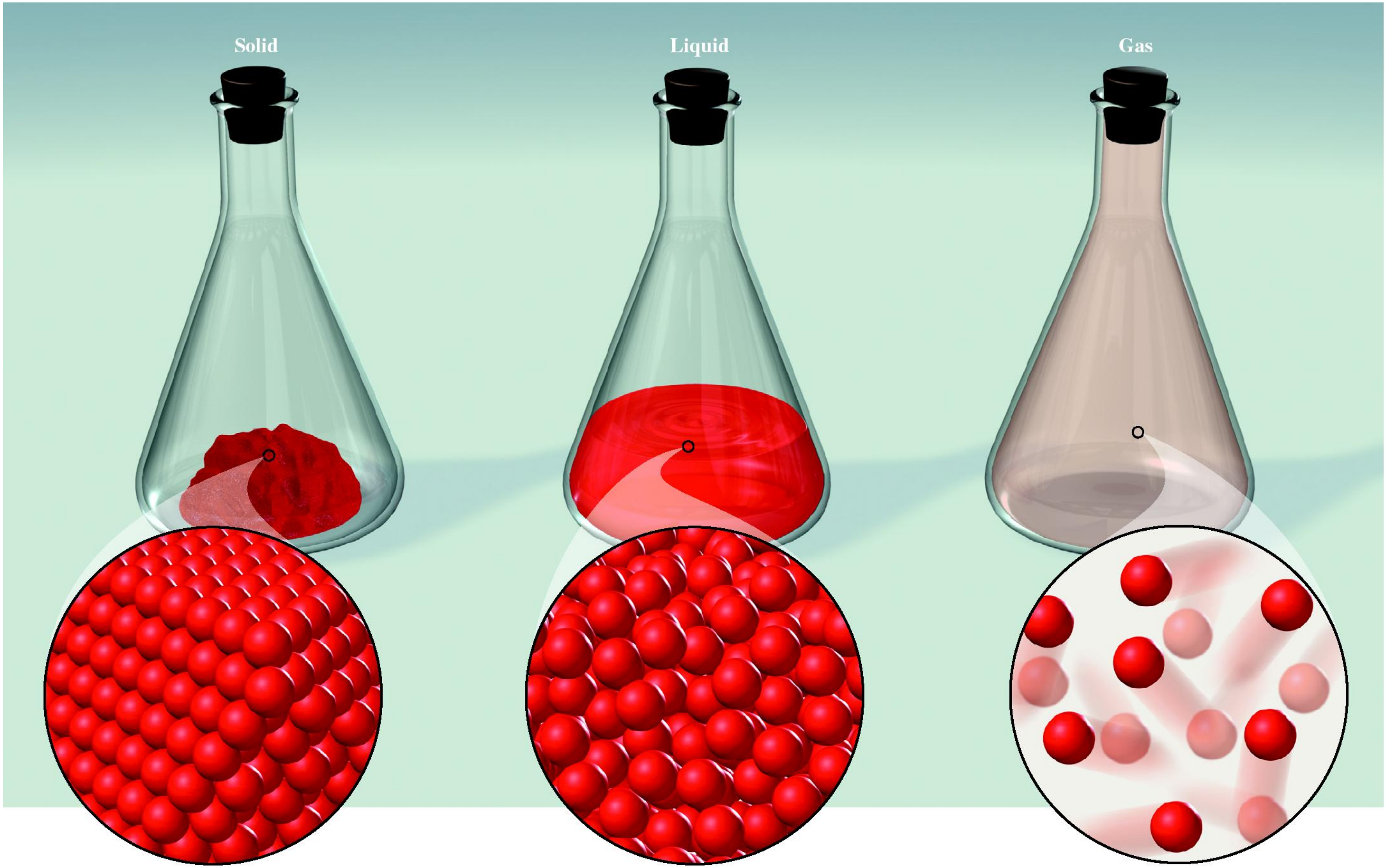
Comparison of the Three States of Matter



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

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

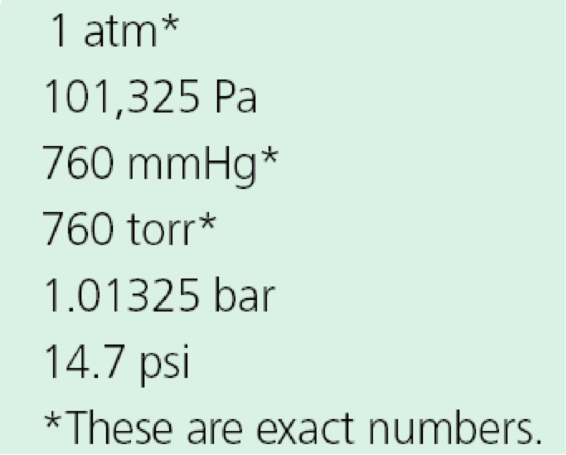
  - ***newton*** (*N*): Unit of force

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

  - ***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.

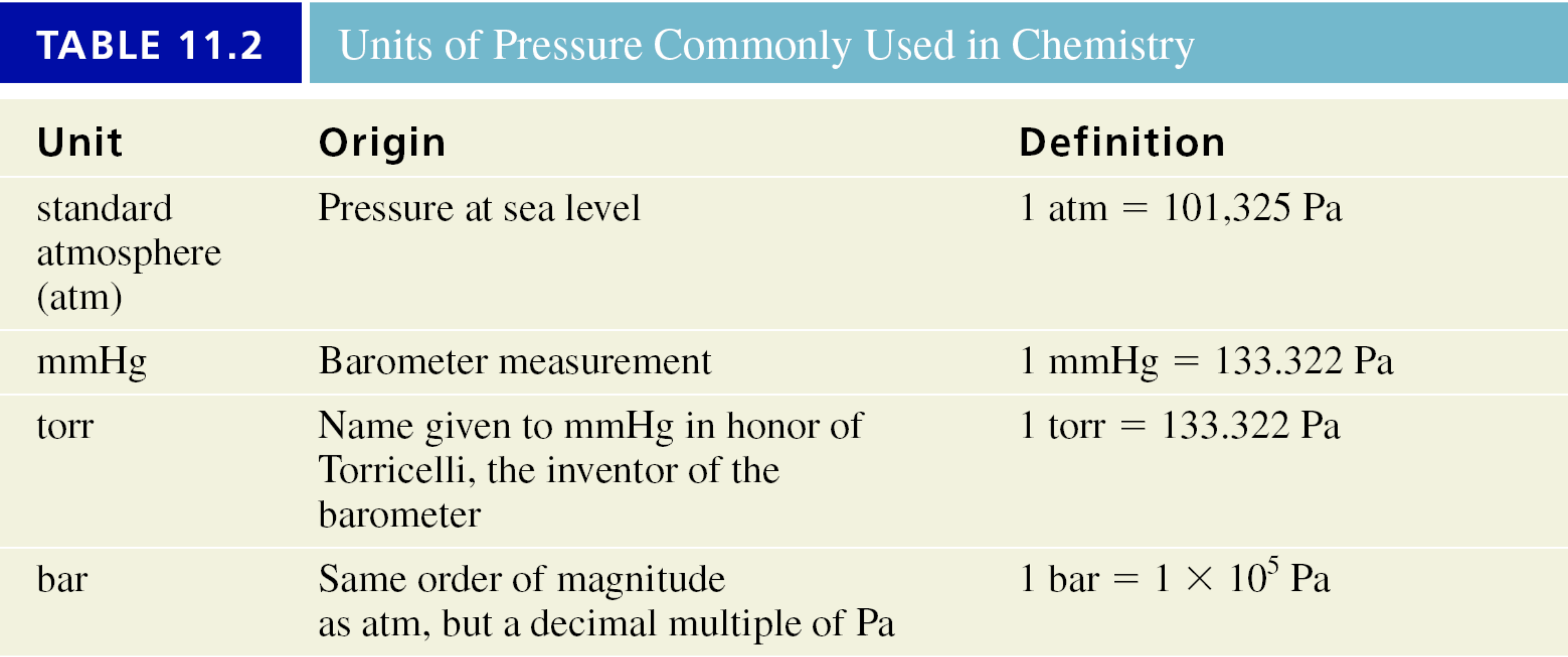


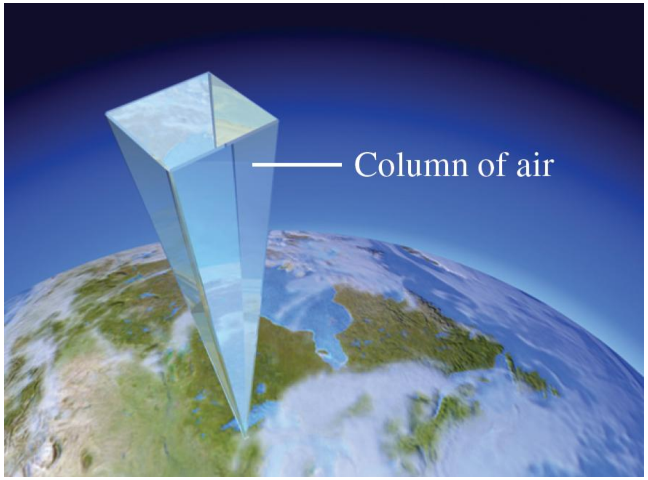
TABLE 11.2 Units of Pressure Commonly Used in Chemistry

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

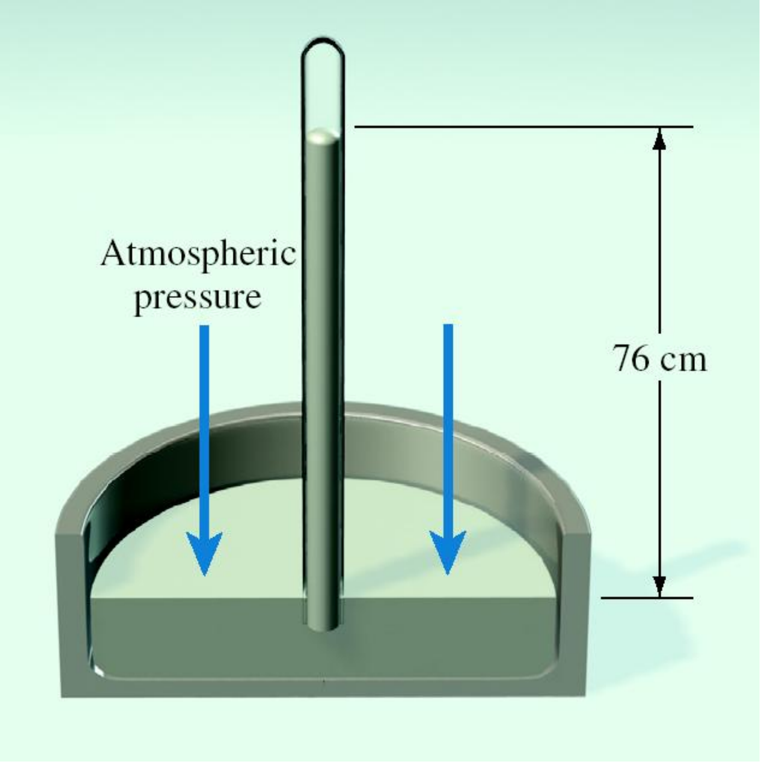
Mass: 1 kg

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

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

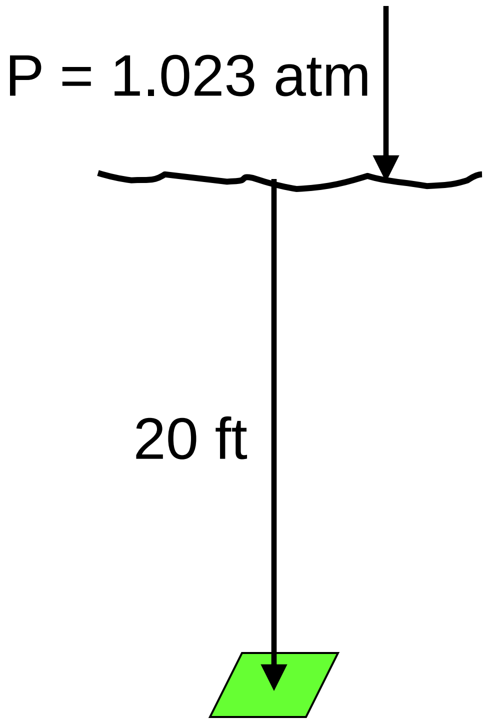
$$\frac{10\ \text{N}}{0.0001\ \text{m}^2} = 1 \times 10^5\ \text{Pa}$$

- 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:



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

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

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

$$\begin{array}{l} 0.5898 \\ \underline{1.023} \\ 1.613\ \mathrm{atm} \end{array}$$

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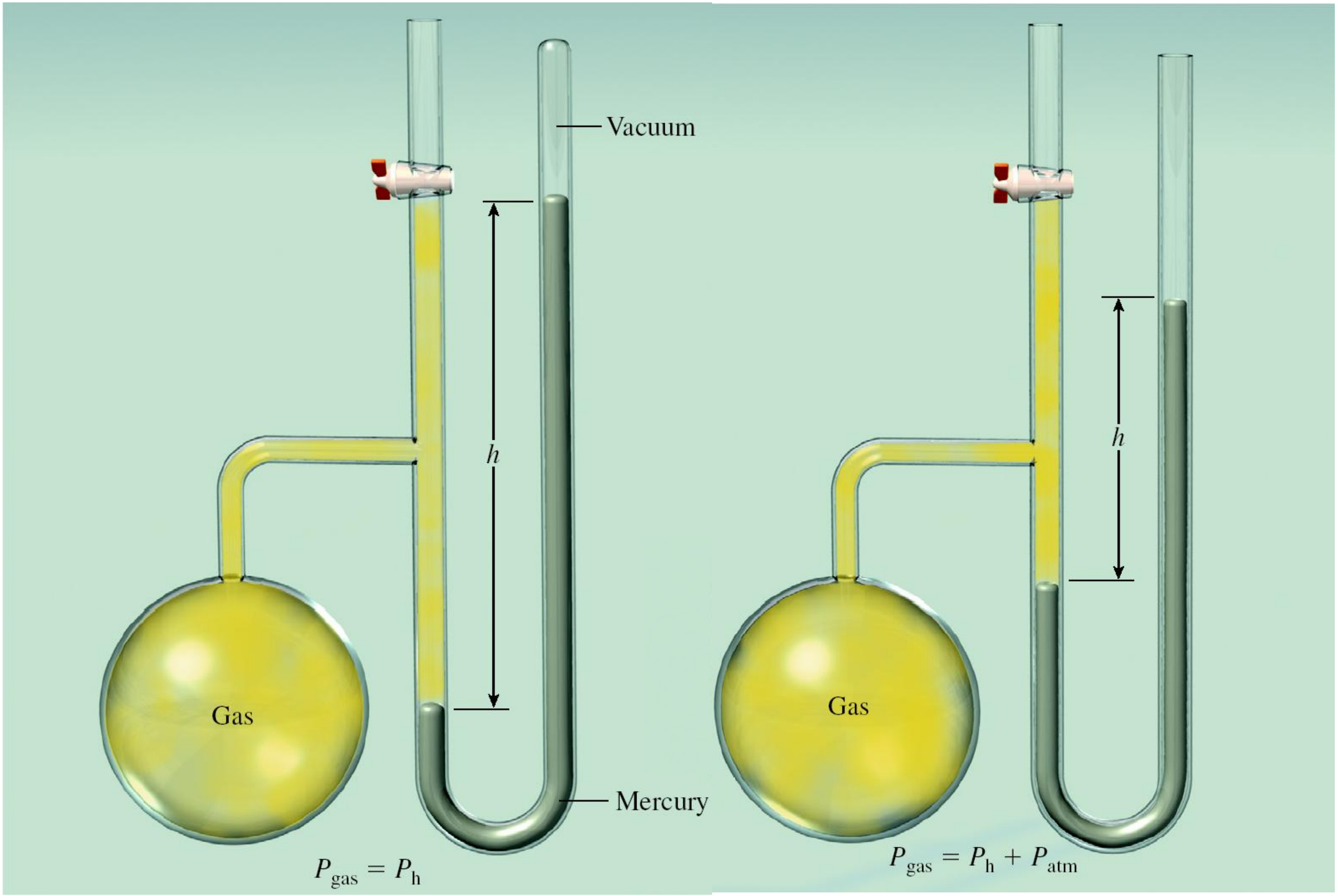
- *A* ***manometer*** is a device used to measure pressures other than atmospheric pressure.
    - Used to measure pressures of gas samples
    - Types
        - Open
        - Closed

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)

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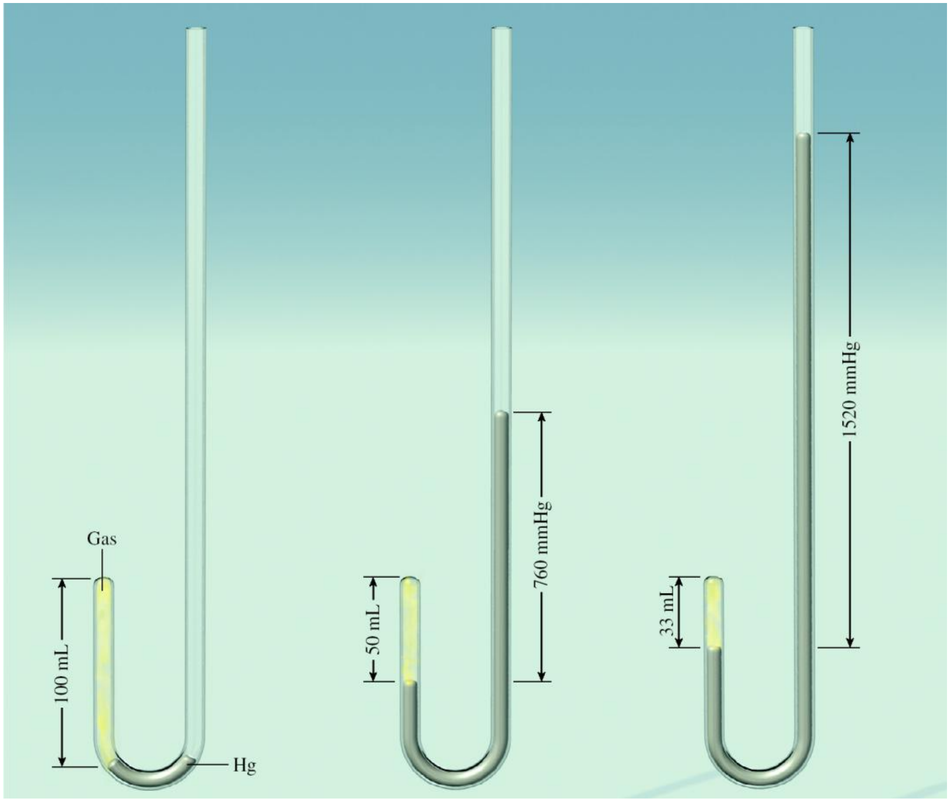
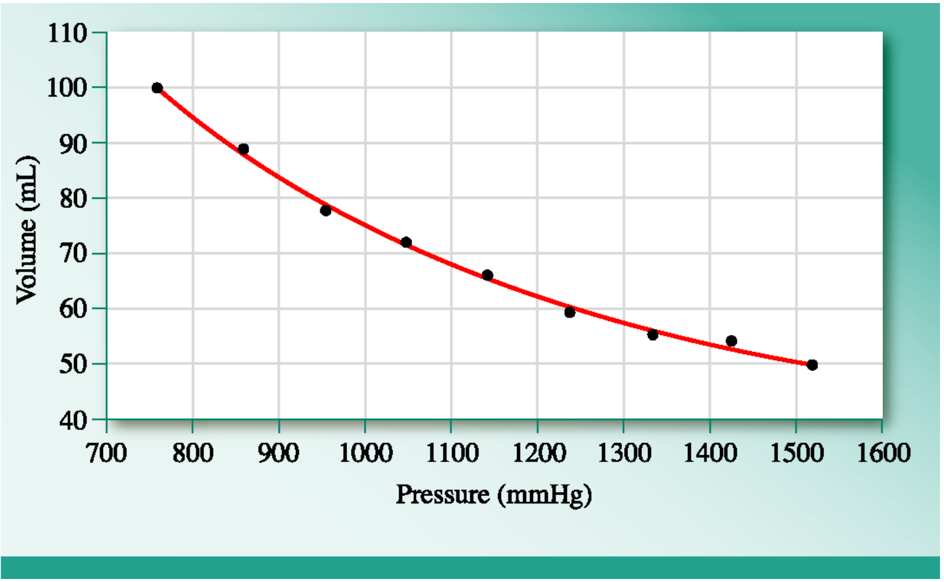
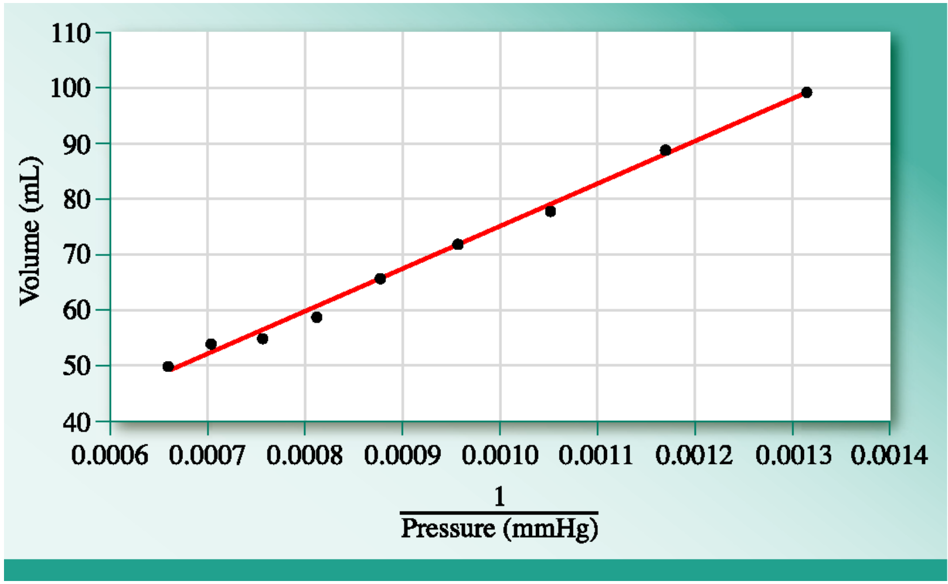
- Boyle's law: pressure-volume relationship at constant temperature

$$P_1V_1=P_2V_2$$



Graphical Expressions of Boyle’s Law





Hyperbola

PV = constant

Straight Line

V = *k* / *P*

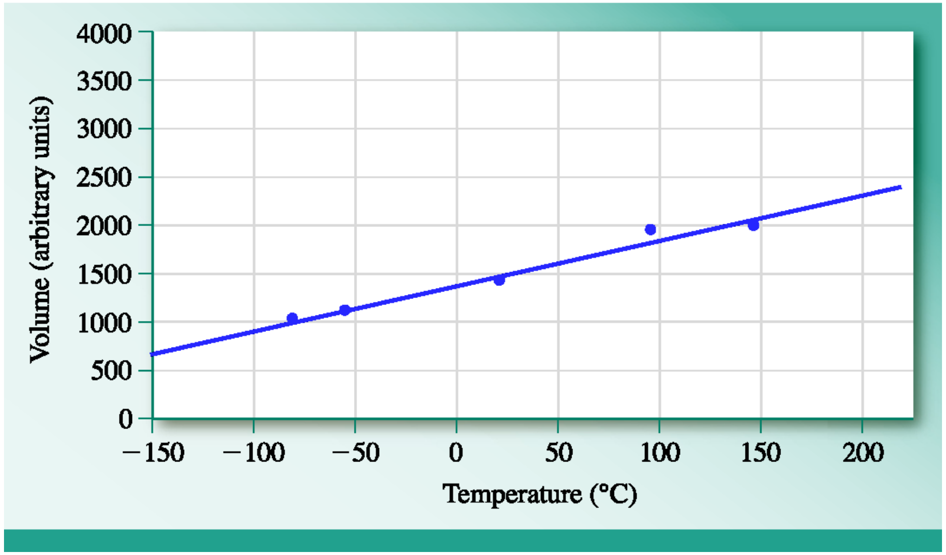
(*y* = *mx* + *b*)

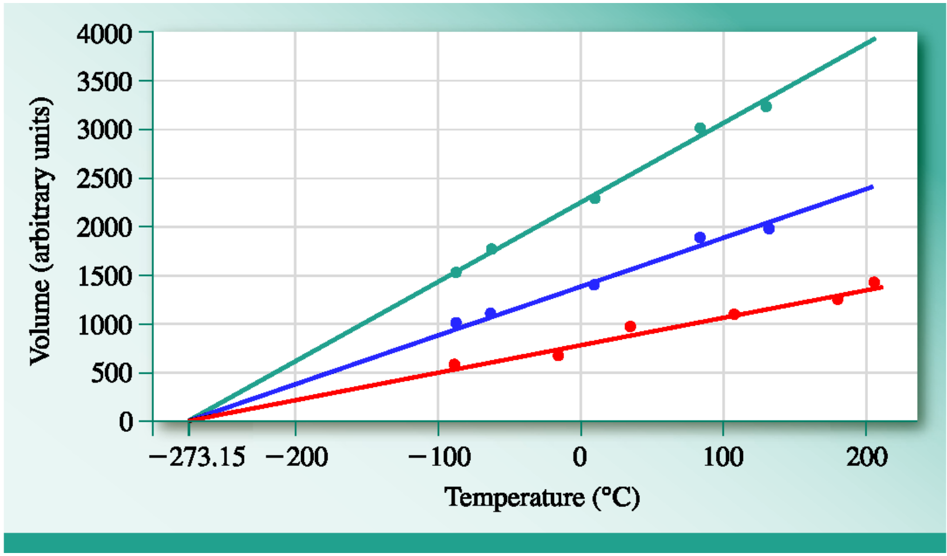
- Charles' and Guy-Lussac's law: temperature-volume relationship at constant pressure

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

Liquid N_2

Graphical Expressions of Charles’ Law





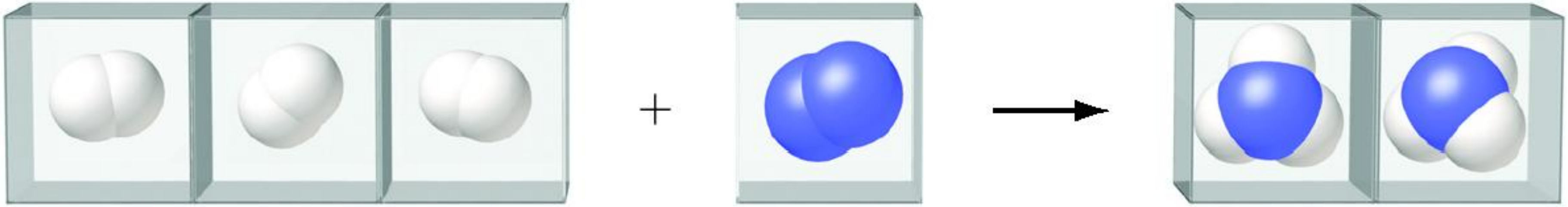
V = constant x *T*

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

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

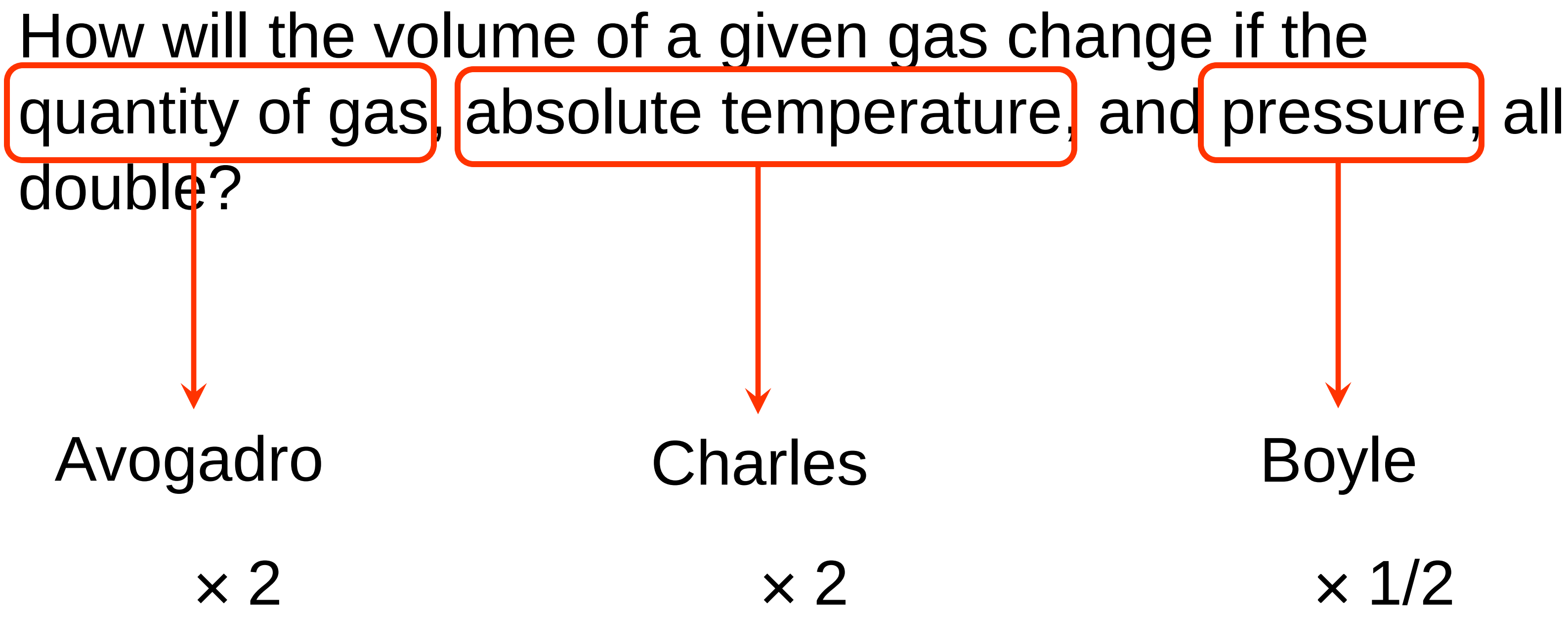
$$3H_2(g) + N_2(g) \longrightarrow 2NH_3(g)$$



3 molecules + 1 molecule → 2 molecules

3 moles + 1 mole → 2 moles

3 volumes + 1 volume → 2 volumes



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

Avogadro

× 2

Charles

× 2

Boyle

× 1/2

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

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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: $V \propto n$

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

- Adding the proportionality constant, *R*

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

$$PV = nRT$$

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TABLE 11.4 Various Equivalent Expressions of the Gas Constant, *R*

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

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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 = ?

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

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

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

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

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

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

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

  - 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?

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

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

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

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

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

$$V_2 = ?$$

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

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

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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

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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

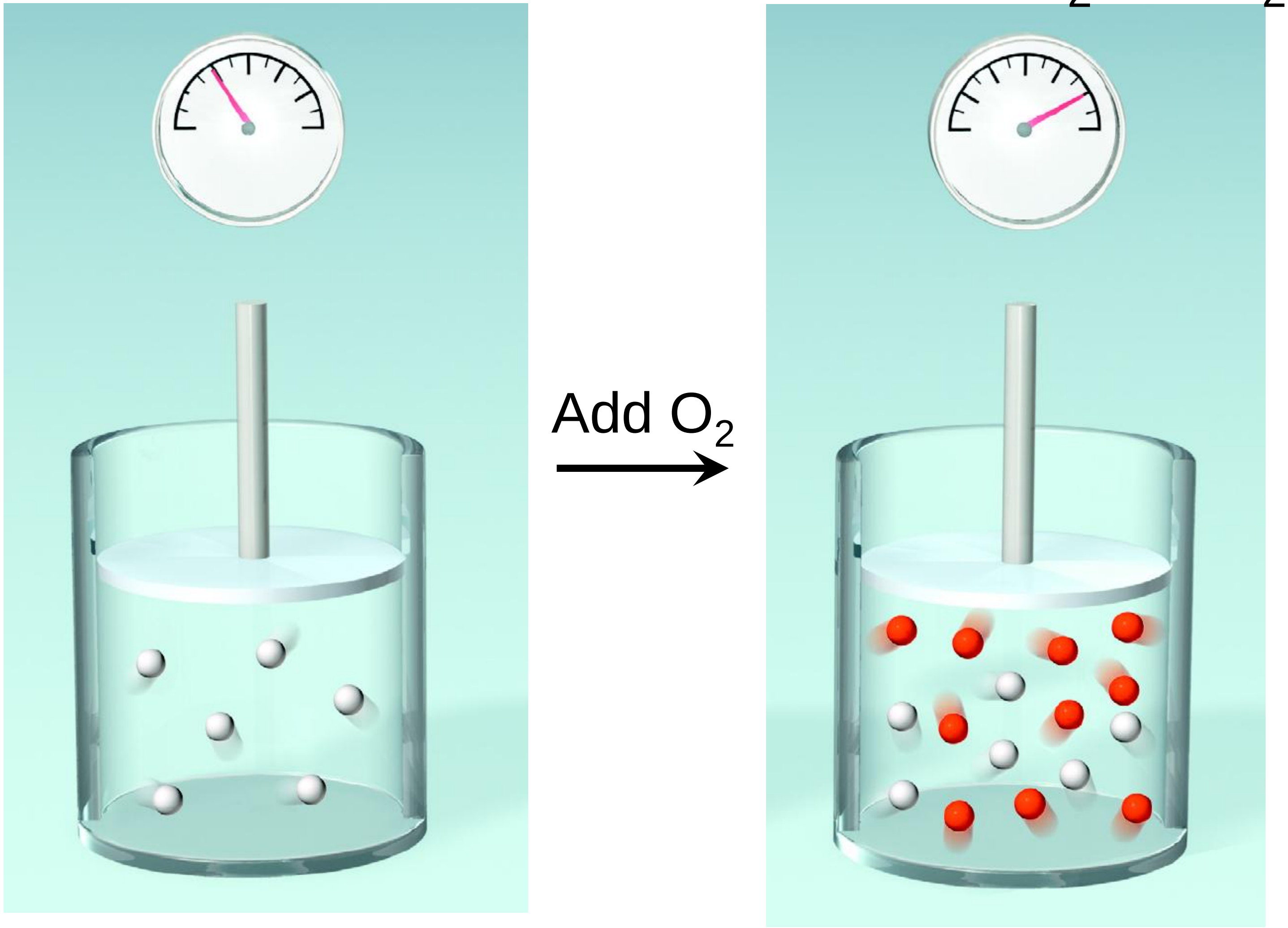
- In gaseous mixtures, each gas behaves as though it occupies the container alone.
  - Assuming no reaction between gases
- ***partial pressure*** (P_i): the pressure exerted by each gas in a gaseous mixture
- Dalton's law of partial pressures

$$P_t = \Sigma P_i$$

Schematic of Dalton’s Law

P_{N_2}

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



$\xrightarrow{\text{Add } O_2}$

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

$$\chi_{\mathrm{i}} = \frac{n_{\mathrm{i}}}{n_{\mathrm{total}}}$$

  - Relation to pressure

$$\chi_{\mathrm{i}} = \frac{P_{\mathrm{i}}}{P_{\mathrm{total}}}$$

$$\chi_{\mathrm{i}} \times P_{\mathrm{total}} = P_{\mathrm{i}}$$

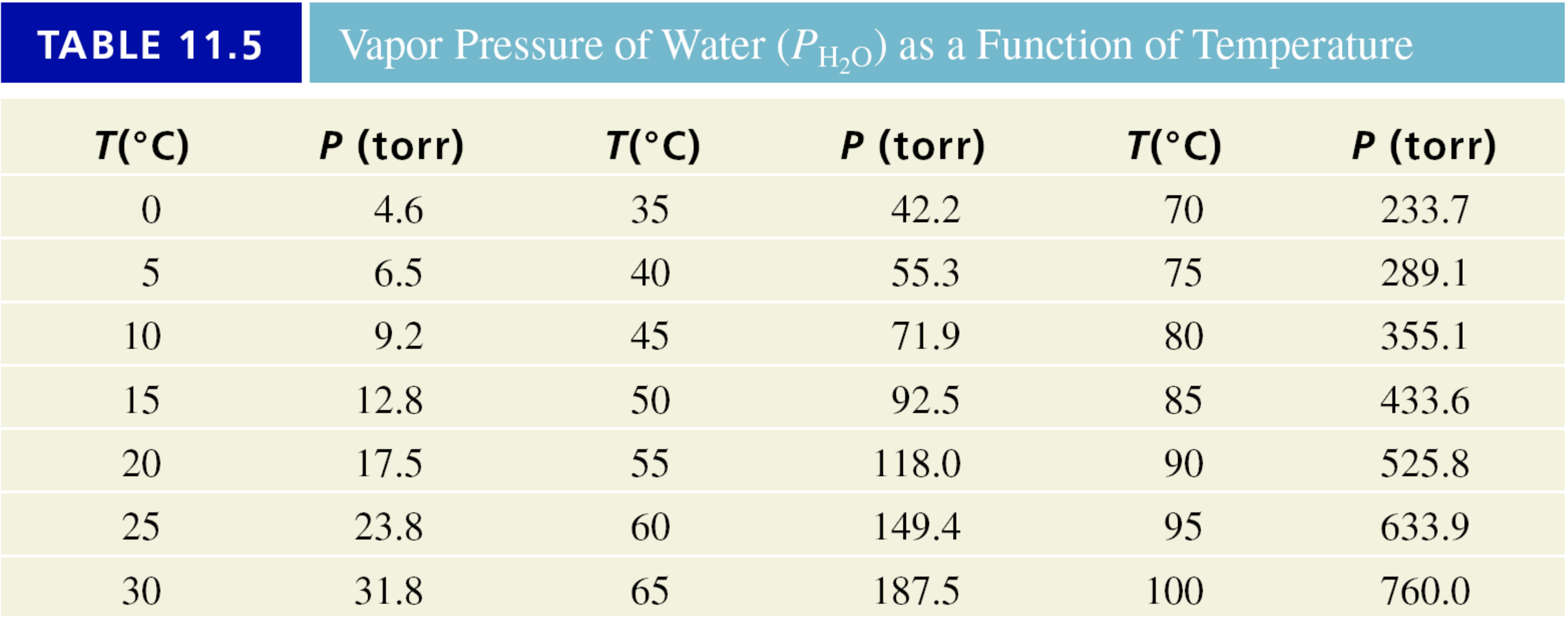


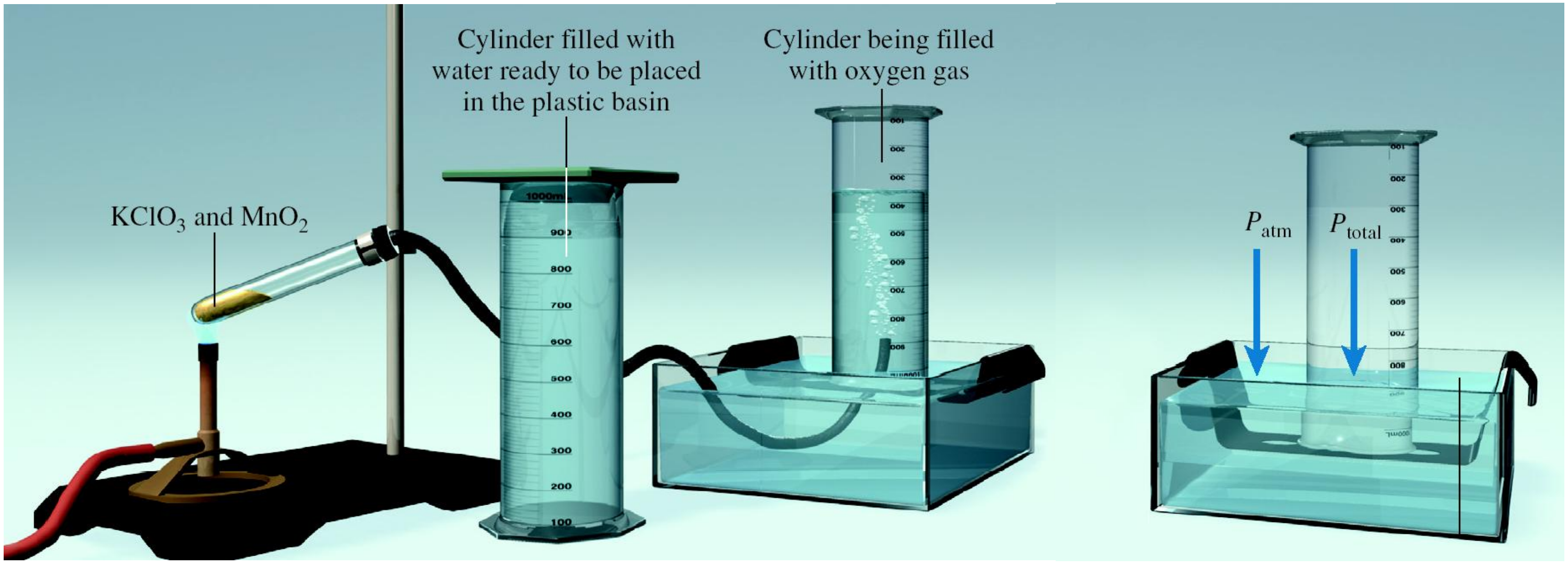
TABLE 11.5 Vapor Pressure of Water (P_{H_2O}) as a Function of Temperature

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.



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

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

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

$T = 22^{o}\text{C} + 273 = 295\text{ K}$

$$n = \frac{PV}{RT}$$

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

$$2\,\text{KClO}_3(s) \rightarrow 2\,\text{KCl}(s) + 3\,\text{O}_2(g)$$

$$1.29\times10^{-2}\text{ mol O}_2\left(\frac{2\text{ mol KClO}_3}{3\text{ mol O}_2}\right)\left(\frac{122.6\text{ g KClO}_3}{1\text{ mol KClO}_3}\right) = 1.06\text{ g KClO}_3$$

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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.

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- 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)

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- 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)

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- Molecular speed
  - ***Root mean square*** (***rms***) ***speed*** (***u*****$_{rms}$**)

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

- For two gases (1 and 2)

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

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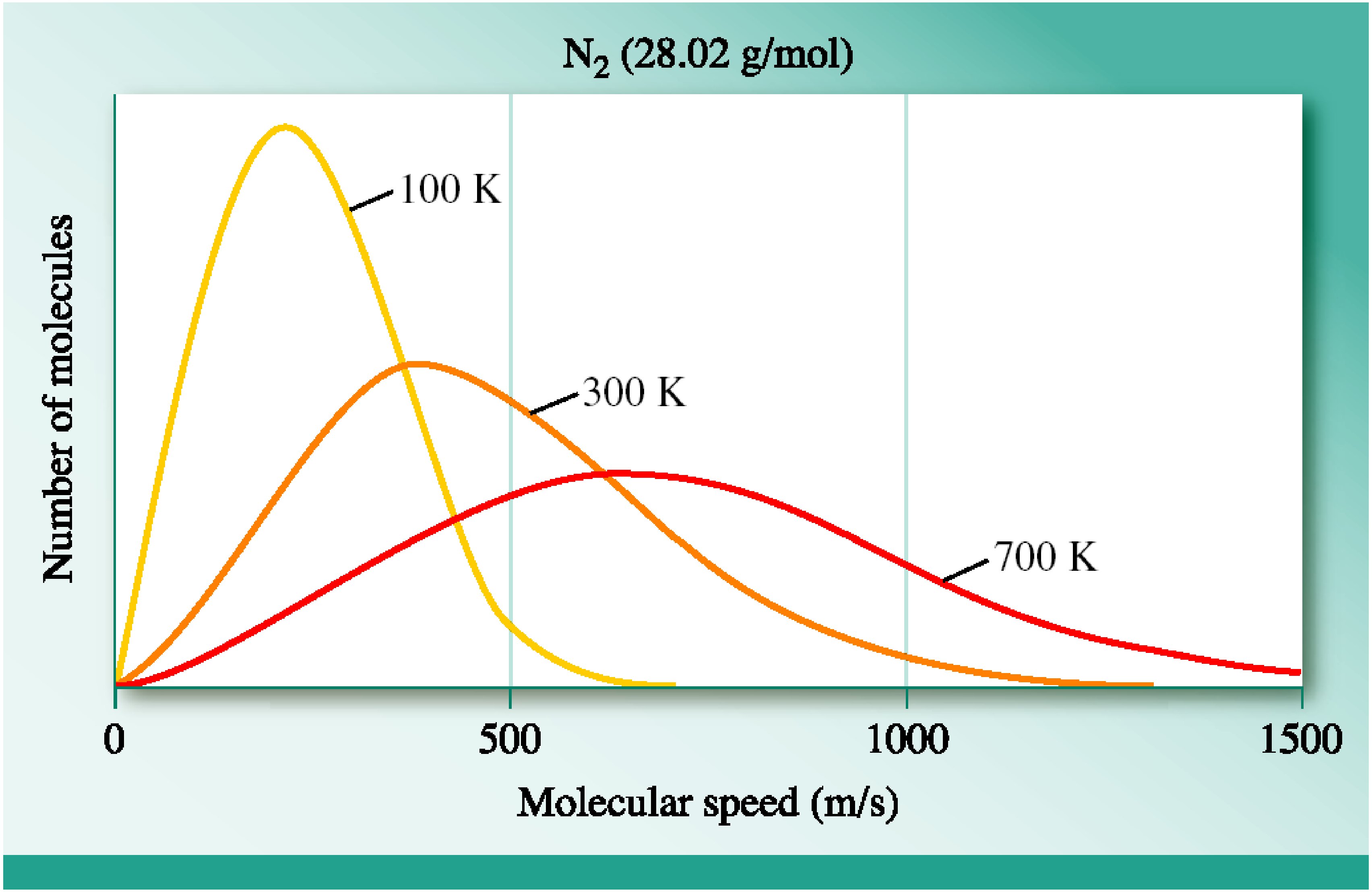
Effect of Temperature on Molecular Speed



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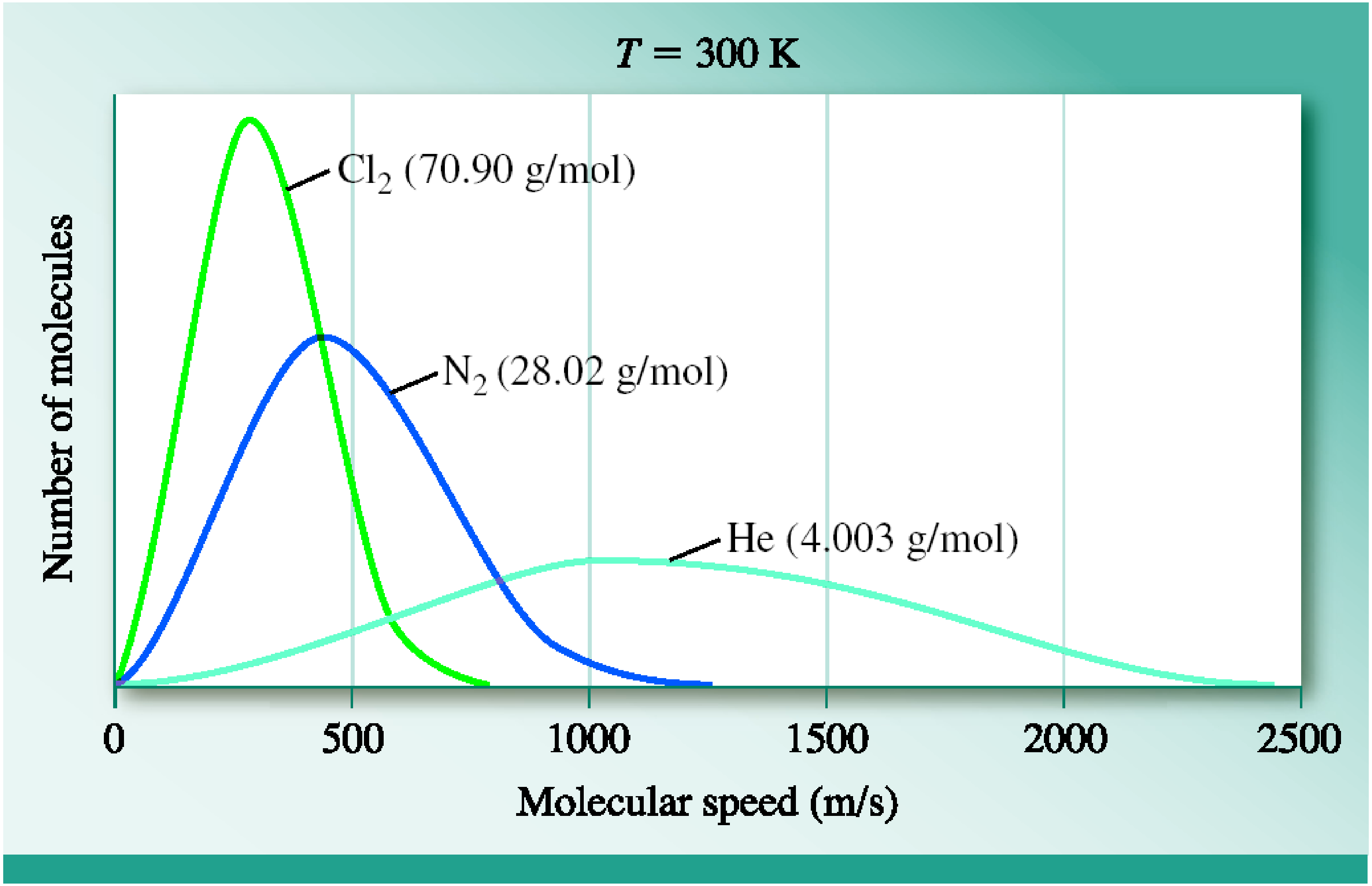
Effect of Molar Mass on Molecular Speed



- 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

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

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

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

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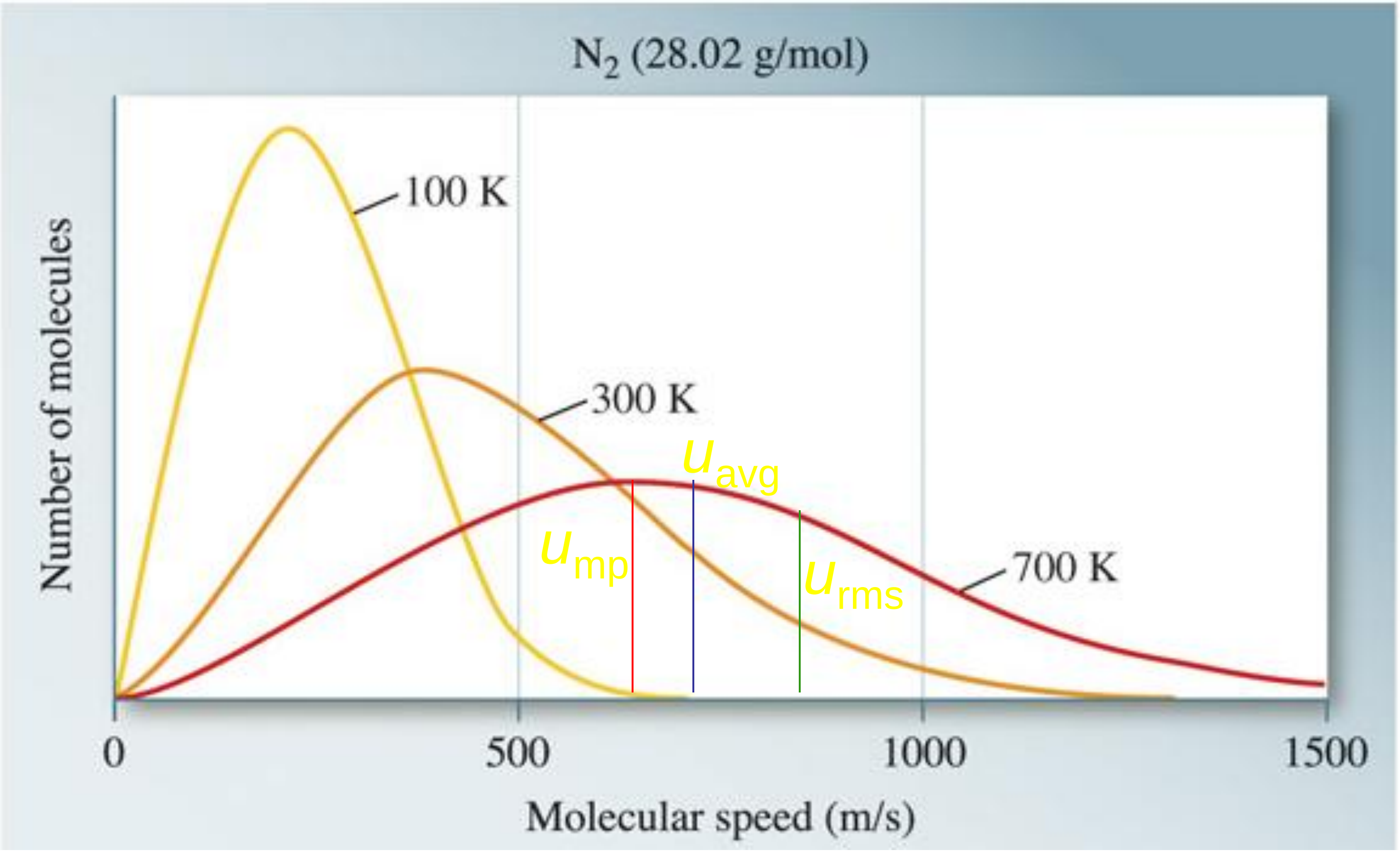
N_2 (28.02 g/mol)
100 K
300 K
700 K
u_{avg}
u_{mp}
u_{rms}
Number of molecules
Molecular speed (m/s)
0
500
1000
1500

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

H_2, CO_2, Ne, NH_3, Cl_2

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

Which one has the highest average kinetic energy?

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

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

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

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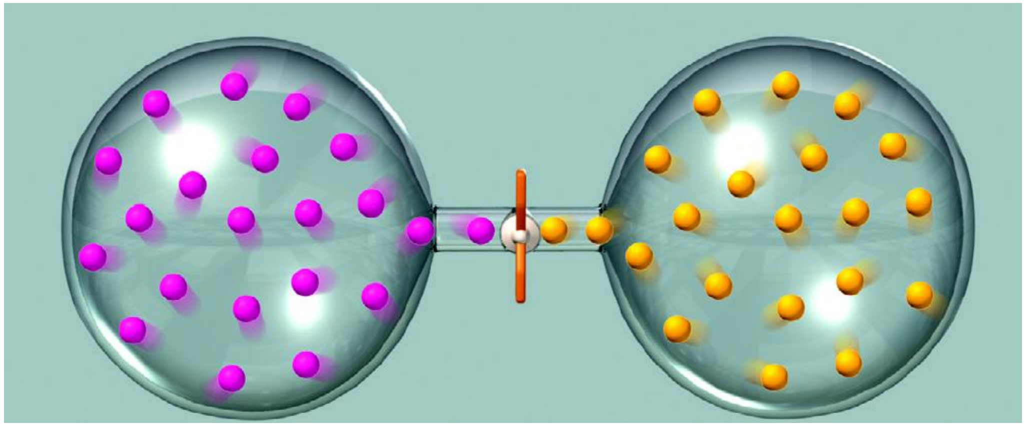
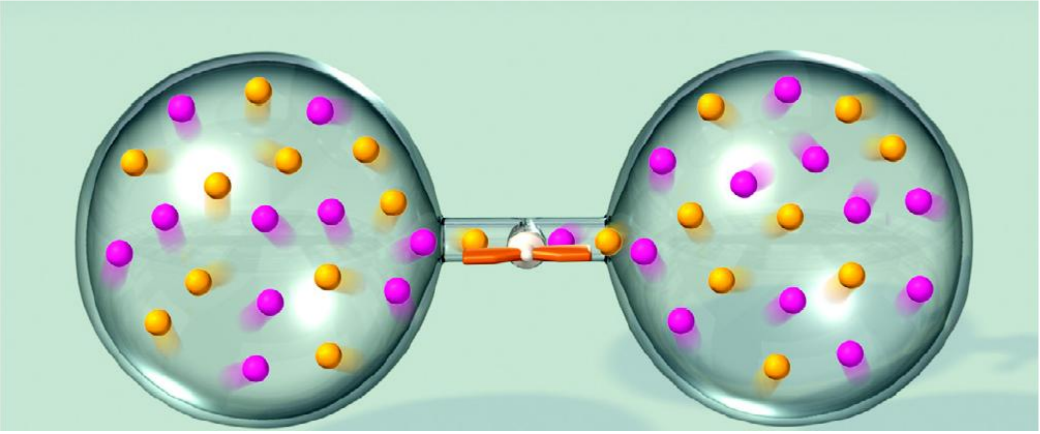
- ***Diffusion***: the mixing of gases as a results of random motion and collisions.

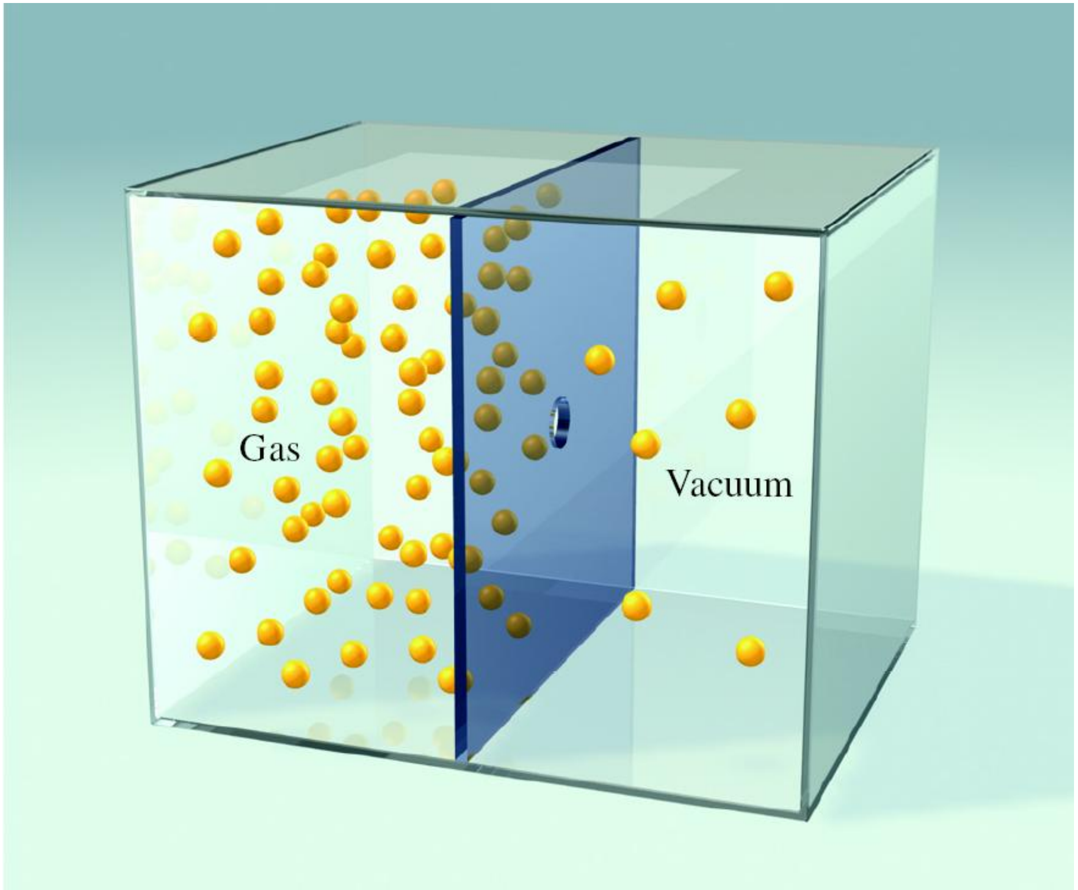


Open valve

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



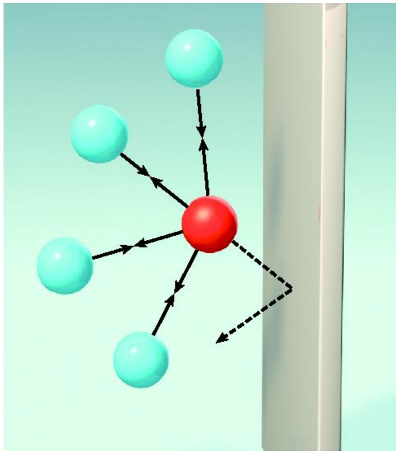
- ***Effusion***: the escape of a gas from a container to a region of vacuum



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

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

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- 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

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- The ideal gas law

$$PV = nRT$$

becomes van der Waal’s equation

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

a and *b* have specific values for each gas

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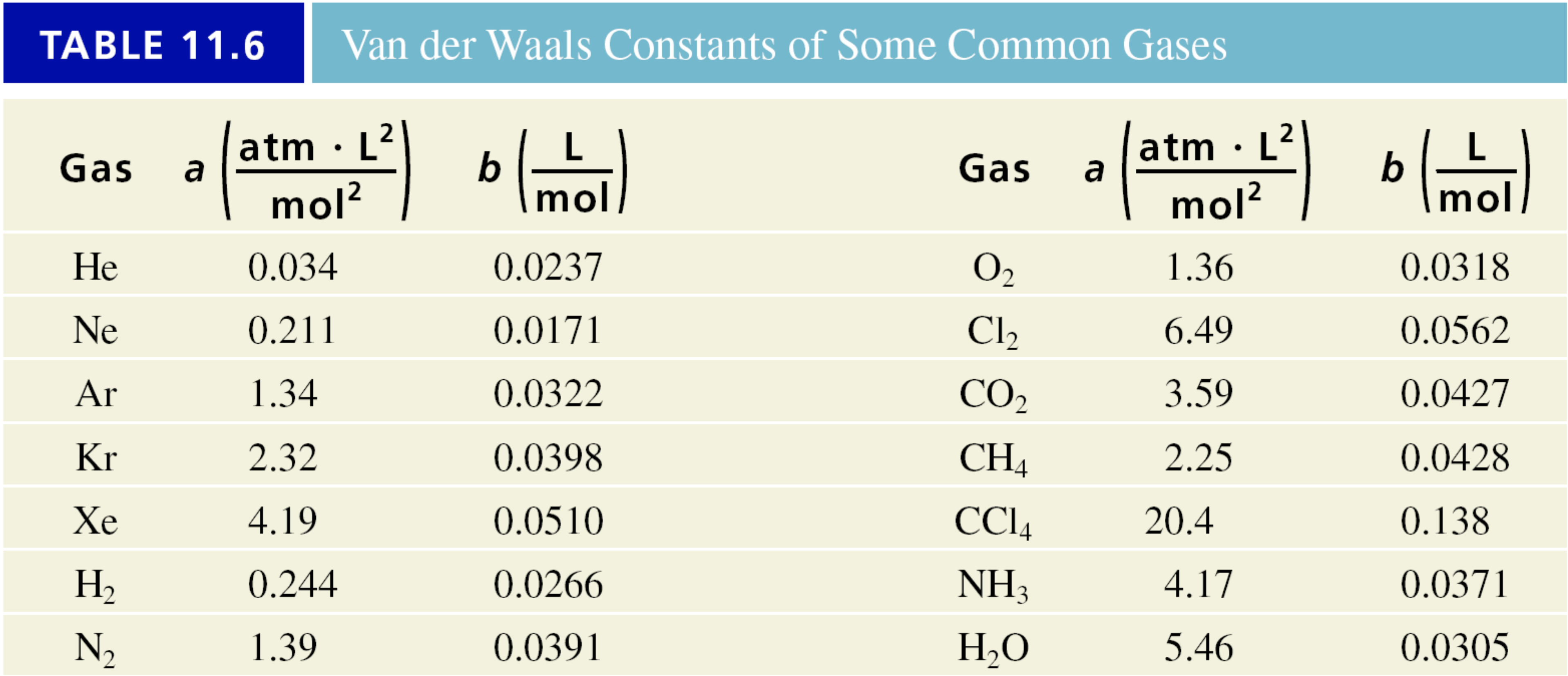

TABLE 11.6 Van der Waals Constants of Some Common Gases

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

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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

- Diffusion and effusion