Chapter 5 (Hill/Petrucci/McCreary/Perry

Gases and Gas Behavior

This chapter deals with gases, including their general properties. We will begin by looking at the underlying theory of gas behavior, the kinetic-molecular theory (KMT), which is a nanoscale treatment of macroscale gas behavior.

Air is so insubstantial that it is difficult to think of it as matter … Air has mass and occupies space; it is matter in the gaseous state.” (Hill, p.169)

General Properties of Gases
1. Molecules of gas are found at large distances from other molecules of gas, when compared to liquids or solids.
2. Gases are fluids – they “flow” with very little frictional resistance from place to place.
3. Gases expand or contract to match the volume of their container (unlike either liquids or solids).
4. The volume of gases is easily reduced (gases can be compressed), since their particles have room to be pushed closer together.
5. When substances that are normally liquids evaporate, the gas formed is called a vapor (“vapor state”).

The Kinetic-Molecular Theory (KMT)
KMT … nanoscale model of gas behavior
- Views gases as large numbers of very small, widely-spaced particles in constant, random translational motion.
- Molecules of gases travel in straight lines and do not interact with each other .. No attractive or repulsive forces between molecules.
- Volume of the gas molecules themselves is negligible … zero?

Gas Pressure
Pressure: force/unit area \( \Rightarrow P = \frac{F}{A} \)

SI Unit: \( F = ma = \text{kg} \cdot (\text{m} \cdot \text{s}^{-2}) = \text{N} \) (newtons) and \( A = l \times w = \text{m} \cdot \text{m} = \text{m}^2 \)
so \( P = \frac{(\text{kg} \cdot \text{m} \cdot \text{s}^{-2})}{\text{m}^2} = (\text{kg} \cdot \text{m} \cdot \text{s}^{-2})/(\text{m}^2) \)
\( P = \frac{(\text{kg} \cdot \text{m} \cdot \text{m}^{-1} \cdot \text{s}^{-2})}{\text{m}^2} = \text{kg} / \text{m} \cdot \text{s}^2 = \text{Pa} \) (pascals)

See also Appendix B.2, p. A-10 (Hill)

Gas Pressure – Unit Conversions
Pressure units: atm, mmHg, torr, Pa, bar, lb/in²
1 torr = 1 mmHg \quad 1 \text{ mb} = 10^{-3} \text{ bar} \quad 1 \text{ atm} = 101,325 \text{ N/m}^2 = 101,325 \text{ Pa} \quad 1 \text{ atm} = 14.70 \text{ lb/in}^2 = 101,325 \text{ kPa}
“Variables of State” for Gases
Question: what variables/physical parameters do we need to completely describe define a gas?
Answer: pressure (P), volume (V), temperature (T) and number of mols of gas (n)

By convention, we frequently use the following units:
Pressure (atmospheres, atm)
Volume (liters, L)
Temperature (kelvins, K)*  *must always use K
Moles (mol)

Named Gas Laws: A Summary
1. Boyle’s Law: pressure and volume relationship
   \[ P \propto \frac{1}{V} \Rightarrow P \cdot V = \text{constant} \] (at constant T, n)
   \[ P_1 V_1 = P_2 V_2 \]
   \[ V \propto T \Rightarrow \frac{V}{T} = \text{constant} \] (at constant P, n)
   \[ \frac{V_1}{T_1} = \frac{V_2}{T_2} \]
3. Avogadro’s Law: volume and moles relationship
   \[ V \propto n \Rightarrow \frac{V}{n} = \text{constant} \] (at constant P, T)
   \[ \frac{V_1}{n_1} = \frac{V_2}{n_2} \]

Gay-Lussac’s Law of Combining Volumes (1811)
Consider the following gas-phase reaction:
\[ 2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(g) \]
Gay-Lussac’s Law says that 2 volumes of H\(_2\) react with 1 volume of O\(_2\) to produce 2 volumes of water vapor.
Gay-Lussac’s Law: volumes of reacting gases are always in ratios of small whole numbers under conditions of constant temperature and pressure

Thus, in the example above, how many liters of H\(_2\) are needed to react with 15.0 L of O\(_2\) at 250°C and 1.0 atm? Answer: 30.0 L (2 x 15.0 L)

An Important Implication of the Avogadro’s Law and Gay-Lussac’s Law Taken Together
Equal volumes of all gases, under the same temperature and pressure conditions, contain the same number of molecules!

Ideal Gases
Gases are real systems … however, we find it useful to postulate an “ideal gas,” one that matches the behavior of described by the KMT.

Definition: STP (standard temperature and pressure)
\[ \Rightarrow 0.0 \text{°C} (273.15 \text{K}) \text{ and 1 atm or 760 Torr (Know this!)} \]

STP conditions: the volume of exactly 1 mol of an ideal gas = 22.41 L (molar volume).

For comparison, actual gas volumes at STP:
\[ \text{H}_2 \text{ 22.43 L} \quad \text{He 22.40 L} \quad \text{CO}_2 \text{ 22.43 L} \quad \text{NH}_3 \text{ 22.09 L} \]
The Ideal Gas Law:
Review: \( V \propto \frac{1}{P} \); \( V \propto T \); \( V \propto n \)

Combining, \( V \propto nT/P \) (or, \( PV \propto nT \))

\( \Rightarrow V = \text{constant} \times nT/P = R \cdot (nT/P) \)

At STP and for 1 mol gas, substituting into the ideal gas equation above and solve for \( R \):

\[ R = \frac{PV}{nT} = \frac{(1.00 \text{ atm} \cdot 22.4 \text{ L})}{(1.00 \text{ mol} \cdot 273 \text{ K})} = 0.0821 \]

\( R = 0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K} \)

Ideal Gas Law Problems

If the number of mols of a gas remain constant,

\( P_1 V_1 / n T_1 = P_2 V_2 / n T_2 \)

\( P_1 V_1 / T_1 = P_2 V_2 / T_2 \) “combined gas law”

Work through Examples 5.4, 5.5, 5.6 and 5.7 on your own.

Exercise 5.4A, p. 178

\( P_1 V_1 / n T = P_2 V_2 / n T \) (T and n constant), so ideal gas law reduces to \( P_1 V_1 = P_2 V_2 \)

Identify initial and final values for variables given:

\( P_1 = 988 \text{ Torr} \quad P_2 = ? \)
\( V_1 = 535 \text{ mL} \quad V_2 = 1.05 \text{ L} \) (1 mol/10 \(^3\) L) = 1.05 \times 10 \(^3\) mL

\( (988 \text{ Torr})(535 \text{ mol}) = P_2 (1.05 \times 10 \(^3\) \text{ mL}) \)

\( P_2 = 503 \text{ Torr} \)

Exercise 5.6A, p. 180

\( P_1 V_1 / n T = P_2 V_2 / n T \) (P and n constant), so ideal gas law reduces to \( V_1 / T_1 = V_2 / T_2 \)

Identify initial and final values for variables given:

\( V_1 = 692 \text{ L} \quad V_2 = ? \)
\( T_1 = 602 + 273 = 875 \text{ K} \quad T_2 = 23 + 273 = 296 \text{ K} \)

\( 692 \text{ L} / 875 \text{ K} = V_2 / 296 \text{ K} \)

\( V_2 = 234 \text{ L} \)

Exercise 5.8A, p. 182

\( \text{C}_3\text{H}_8 \) (44.09 g/mol)

\( PV = nRT \) with \( P, V \) and \( T \) given, at STP

Need to find mass of \( \text{C}_3\text{H}_8 \) … we can do this if we first find mol \( \text{C}_3\text{H}_8 \). So only unknown in ideal gas equation is \( n \):

Identify values for variables given

\( P = 1.00 \text{ atm} \) (STP) \quad \( T = 273 \text{ K} \) (STP)
\( V = 50.0 \text{ L} \quad n = ? \)

\( (1.00 \text{ atm})(50.0 \text{ L}) = n(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(273 \text{ K}) \)
\( n = (2.231 \text{ mol}) \times (44.09 \text{ g/mol}) = 98.4 \text{ g} \ \text{C}_3\text{H}_8 \)

\( \text{g} \ \text{C}_3\text{H}_8 = 98.4 \text{ g} \ \text{C}_3\text{H}_8 \)
See Example 5.10 and Work Through Exercise 5.10A p. 185
See which variables are given: P, V, T. ⇒ find n
PV = nRT \hspace{1cm} R = 0.0821 \text{ L·atm/mol·K}

Identify values for variables given: P = 3.15 atm, V = 35.0 L, T = 852 K, n = ?
(3.15 atm)(35.0 L) = n(0.0821 \text{ L·atm/mol·K})(852 K)

\[ n = 1.57 \text{ mol N}_2 \]

**Determination of Molecular Mass from Ideal Gas Law**

PV = nRT \hspace{1cm} R = 0.0821 \text{ L·atm/mol·K} \hspace{1cm} n = \frac{PV}{RT}

See Example 5.12, p. 187

P = 0.968 atm \hspace{1cm} T = 289 K \hspace{1cm} m = 0.550 \text{ g}

V = 0.200 L \hspace{1cm} n = ?

(0.968 atm)(0.200 L) = n(0.0821 \text{ L·atm/mol·K})(289 K)

n = 0.00816 \text{ mol}

\[ M = 0.550 \text{ g} / 0.00816 \text{ mol} = 67.4 \text{ g/mol} = 67.4 \text{ u} \]

**Ideal Gas Law Problems – Gas Densities**

From ideal gas law, PV = nRT

Then, \hspace{1cm} \frac{n}{V} = \frac{P}{RT} \hspace{1cm} \text{but,} \hspace{1cm} n = \left( \frac{m}{1/M} \right), \text{ where } m = \text{ mass, g}; M = \text{ molar mass, g/mol}

So, \hspace{1cm} \left( \frac{m}{1/M} \right)/V = \frac{P}{RT}

\[ m/V = \frac{\text{d} = \text{PM/RT}}{\text{d} = \text{PM/RT}} \]

See Example 5.14 and Exercises 5.14A and 5.14B, p. 189, Hill

**Exercise 5.14A**

Calculate the density of C$_2$H$_6$ gas at 15°C and 748 Torr.

**Solution.** \hspace{1cm} d = PM/RT \hspace{1cm} R = 0.0821 \text{ L atm/mol K}

P = 748 Torr(1 atm/760 Torr) = (748/760)atm

T = 15 + 273 = 288 K

M = 30.07 g/mol

\[ d = \frac{(748/760) \text{ atm} \cdot 30.07 \text{ g/mol}}{[0.0821 \text{ L atm/mol K} \cdot 288 \text{ K})} \]

\[ d = 1.25 \text{ g/L} \]

**Exercise 5.14B**

Calculate the molar mass of C$_x$H$_y$ gas at 20.0°C and 762 Torr if its density is 2.42 g/L.

**Solution.** \hspace{1cm} d = PM/RT \hspace{1cm} R = 0.0821 \text{ L atm/mol K}

P = 762 Torr(1 atm/760 Torr) = (762/760)atm

T = 20.0 + 273.15 = 293.15 K

M = ??

\[ 2.42 \text{ g/L} = \frac{(762/760) \text{ atm} \cdot M}{[0.0821 \text{ L atm/mol K} \cdot 293.2 \text{ K})} \]

\[ M = 58.1 \text{ g/mol} \]
Exercise 5.14B
What is the molecular formula for the gas?
Solution. Gas must have stoichiometry $C_nH_{2n+2}$ See p. 59, Hill

\[
\begin{align*}
n = 1 & \quad CH_4 & \quad 16.0 \text{ g/mol} \\
n = 2 & \quad C_2H_6 & \quad 30.1 \text{ g/mol} \\
n = 3 & \quad C_3H_8 & \quad 44.1 \text{ g/mol} \\
n = 4 & \quad C_4H_{10} & \quad 58.1 \text{ g/mol}
\end{align*}
\]

Gas Law Problems – Gas Phase Reactions
Balanced equations involving gaseous species and the gas laws … Gay-Lussac’s Law and Ideal Gas Law
See Example 5.16, p. 191, Hill

Now let’s work Exercise 5.16A
Volume of $O_2$ gas required to just react with 0.556 L of $C_3H_8$ gas at same temperature and pressure.
Solution: Use Gay-Lussac’s Law since this is a reaction at constant temperature and pressure.

Balance Equation: $C_3H_8(g) + 5 O_2(g) \rightarrow 3 CO_2(g) + 4 H_2O(g)$

\[
1 \text{ mol } C_3H_8 = 5 \text{ mol } O_2 \quad \text{Gay-Lussac’s Law implies mol ratio = volume ratio}
\]

\[
(5 \text{ mol } O_2/1 \text{ mol } C_3H_8) = (? \text{ L } O_2/0.556 \text{ L } C_3H_8)
\]

? L $O_2 = (0.556 \text{ L } C_3H_8)((5 \text{ mol } O_2/1 \text{ mol } C_3H_8)$

? L $O_2 = 2.78 \text{ L}$

Gas Phase Reactions – Ideal Gas Law (pp. 192-193)
Balanced equations involving gaseous species and the ideal gas law …

See Example 5.17, p. 192, Hill

Work Exercise 5.17A .. in class
$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ (balanced!)

Strategy: First, convert kg $CaCO_3$ to mols $CaCO_3$; then mol $CaCO_3$ to mol $CO_2$

\[
\begin{align*}
\text{mol } CO_2(g) &= (45.8 \times 10^3 \text{ g } CaCO_3)(1 \text{ mol } CaCO_3/100.09 \text{ g } CaCO_3) \\
&\quad \times (1 \text{ mol } CO_2/1 \text{ mol } CaCO_3) = 457.6 \text{ mol}
\end{align*}
\]

Next, convert mol $CO_2$ to L $CO_2$ using ideal gas relation: $PV = nRT$ … list what we know …
P = (754/760) atm \\
T = 825 + 273 = 1098 K \\
n = 457.6 \text{ mol} \\
R = 0.0821 \text{ L atm/mol K}

\[
(754/760)\text{atm}\cdot V = (457.6 \text{ mol})(0.0821 \text{ L atm/mol K})(1098 \text{ K})
\]

\[
L \text{ CO}_2(g) = 4.16 \times 10^4 \text{ L}
\]
Gas Mixtures – Dalton’s Law of Partial Pressures
Now see Exercise 5.19B, p. 195
In our example above, \( P_{\text{total}} = P_{\text{N}_2} + P_{\text{O}_2} + P_{\text{Ar}} + P_{\text{CO}_2} \)

We can calculate the partial pressure using the ideal gas law .. note that partial pressure units are the normal pressure units we’ve used before, mmHg or atm or Torr or ….?

See Example 5.18, p. 194, Hill.

Gas Mixtures – Mole Fractions
It is useful to define a quantity called the mole fraction, \( X_i \). The mole fraction of a gas is simply the fraction of that type of molecule in the mixture.

Operational Strategy: calculating mole fractions:
1. Calculate mols of all species in the mixture
2. Add the mols to get total mols in the mixture (\( n_{\text{total}} \))
3. Divide the mol of each gas by the total to get its mol fraction (\( X_i \)), where \( X_i = n_i/n_{\text{total}} \)

For nonreacting gases, the pressure fraction is the mol fraction:
\( P_i/P_{\text{total}} = X_i \) or, \( P_i = X_i \cdot P_{\text{total}} \)

See Example 5.19, p. 195

Gas Mixtures – Dalton’s Law of Partial Pressures
Now see Exercise 5.19B, p. 195
This mixture consists of four gases … note that we are given the partial pressure of each gas.

Strategy: Sum the partial pressures to get the total pressure; then divide each partial pressure by the total to get mol fractions. Need to use ideal gas law to get partial pressure for butane:
\( PV = (m/M)RT \)

\( \text{C}_4\text{H}_{10} \):
\( P(75.0 \text{ L}) = (10.5/58.1)\text{mol}(0.0821 \text{ L atm/mol K})(296.6 \text{ K}) \)
\( P = 0.0586 \text{ atm}(760 \text{ Torr/atm}) = 44.5 \text{ Torr} \)

\( P_{\text{total}} = 505 + 201 + 43 + 44.5 = 793.5 \text{ Torr} \)

\( P(\text{CH}_4) = (505/793.5) = 0.636 \)
\( P(\text{C}_2\text{H}_6) = (201/793.5) = 0.253 \)
\( P(\text{C}_3\text{H}_8) = (43/793.5) = 0.054 \)
\( P(\text{C}_4\text{H}_{10}) = (44.5/793.5) = 0.056 \)

Check: \( \sum P_i = 0.636 + 0.253 + 0.054 + 0.056 = 0.999 \equiv 1.000 \)
Dalton’s Law of Partial Pressures – Collection of Gases Over Water
Water vapor is just another gas … water vapor has a vapor pressure (partial pressure) that increases with temperature … see handout … the vapor pressure for water equals exactly 1.00 atm (760 Torr) at its normal boiling point of 100 °C.

We can collect gases over water, by displacement of water from a closed container, if the gases don’t dissolve in water. When we do, we can calculate the partial pressure of the gas from

\[ P_{\text{total}} = P_{\text{gas}} + P_{\text{water vapor}} \]

which rearranges to

\[ P_{\text{gas}} = P_{\text{total}} - P_{\text{water vapor}} \]

Example 5.21, p. 197, Hill
Here, \( P_{\text{total}} = 742 \) Torr and \( P_{\text{water}} = 21.1 \) Torr

so, \( P(\text{H}_2) = 742 - 21.1 = 721 \) Torr

Distribution of Molecular Speeds
Figure 5.17, p. 200, Hill
In (a), average speed increases as molar mass of the gas decreases; in (b), the average speed of \( \text{O}_2 \) molecules increases with increasing temperature.

Diffusion of Gases
Figure 5.18, p. 201, Hill
diffusion: the mixing of molecules of two or more substances (liquids or gases) as a result of random translational motion of the molecules

Effusion of Gases
Figure in right margin, p. 201, Hill
effusion: the process in which gas molecules escape from a closed container through a very small hole
the rate of effusion is inversely proportional to the square root of the molar mass or the density of the gas (Hill, Eq. 5.24, p. 201) … see equation below

\[ \frac{\text{effusion rate for gas 1}}{\text{effusion rate for gas 2}} = \sqrt{\frac{M_2}{M_1}} \]

Real Gases (As Opposed to Ideal Gases)
Figure 5.19, p. 203, Hill
The effects of intermolecular forces on the pressure term in the ideal gas equation – attractive forces slow down molecules and reduce pressure – need to correct by adding to pressure…

Ideal Gas Law: \( PV = nRT \)
van der Waals equation: \( (P + n^2a/V^2)(V - nb) = nRT \)
where \( a \) and \( b \) are called van der Waals constants and are unique for each gaseous compound
See Table 5.5, p. 204, Hill

\( n^2a/V^2 \) - additive term to correct for loss of pressure due to molecular attractions in real gases
\(- nb\) - a subtractive term in real gases used to correct for loss of “free “ container volume due to actual volume of the molecules themselves