CHE 131

Lecture 25 – Gas density, partial pressures, real gases

Prof. Wong


Combined Gas Law

At constant mass of gas

\[ V \propto \frac{T}{P} \]

\[ V = d \times \left( \frac{T}{P} \right) \]

where \( d \) is a proportionality constant

\[ \frac{(VP)}{T} = d \]

\[ \frac{V_1P_1}{T_1} = \frac{d}{T_1} = \frac{V_2P_2}{T_2} \]

\[ \frac{V_1P_1}{T_1} = \frac{V_2P_2}{T_2} \]
Ideal Gas Law

\[ V \propto \frac{(n \times T)}{P} \]
\[ V = \frac{R}{P} \times \frac{(n \times T)}{P} \]

where \( R \) is proportionality constant

\[ P \times V = n \times R \times T \]

Conditions at 0°C and 1 atm are referred to as standard temperature and pressure conditions (STP).
How does Kinetic Molecular Theory account for the ideal gas law?

**Boyle’s:** Decreasing V increases the frequency of particle collisions with the wall, increasing P.

**Charles’s:** Increasing T increases the speed of particles. P, V term must increase to maintain constant P.

**Avogadro’s:** Increasing quantity of gas increases the frequency of particle collisions with the wall.

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R – universal gas constant, same for all gaseous substances!

**Ideal Gas Constant**

<table>
<thead>
<tr>
<th>TABLE 10.4</th>
<th>Values of $R$, in Different Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R = 0.08206 \text{ L atm} \text{ mol}^{-1} \text{ K}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$R = 62.36 \text{ torr L} \text{ mol}^{-1} \text{ K}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$R = 8.314 \text{ kPa dm}^{-3} \text{ mol}^{-1} \text{ K}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$R = 8.314 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$</td>
<td></td>
</tr>
</tbody>
</table>
Example: What volume will 24.0 g O₂ (MM 32.0) occupy at 25°C and a pressure of 0.888 atm?

\[ n = \frac{(24.0 \text{ g})(1 \text{ mol})}{(32.0 \text{ g})} = 0.750 \text{ mol} \]

\[ V = \frac{nRT}{P} = \frac{(0.750 \text{ mol})(0.08206 \text{ L atm/mol K})(298\text{K})}{0.888\text{atm}} \]

\[ = 20.7 \text{ L} \]

Review:

Does volume of balloon increase or decrease as it ascends into the troposphere?
Molar Mass from Gas Density

gas density = \#g/V = d

PV = nRT

where n = \#g/MM

PV = (\#g/MM) \times RT

MM = (\#g \times R \times T)/(P \times V)

MM = (\#g/V) \times ((R \times T)/P) = (d \times R \times T)/P

Dalton’s Law of Partial Pressures

The total pressure of a mixture of gases is equal to the sum of the pressures of the individual gases (partial pressures).

\[ P_T = P_1 + P_2 + P_3 + P_4 + \ldots \]

where

- \( P_T \rightarrow \) total pressure
- \( P_1 \rightarrow \) partial pressure of gas 1
- \( P_2 \rightarrow \) partial pressure of gas 2
- \( P_3 \rightarrow \) partial pressure of gas 3
- \( P_4 \rightarrow \) partial pressure of gas 4
Dalton’s Law

- Boyle’s Experiments were conducted with air.
- Composition ~ 80% N₂, 20% O₂
- How does each contribute to the total pressure?

$$P_{\text{total}} = \frac{n_{\text{total}} RT}{V} = \left( \frac{n_{\text{O}_2} + n_{\text{N}_2}}{V} \right) RT$$

$$= \frac{n_{\text{O}_2} RT}{V} + \frac{n_{\text{N}_2} RT}{V} = P_{\text{O}_2} + P_{\text{N}_2}$$

- **Dalton’s Law of Partial Pressures:**
  $$P_{\text{total}} = \sum_i P_i = P_1 + P_2 + P_3 + \ldots$$
- $P_i$ is termed the **partial pressure** of component i
• We often know the composition and total pressure, so how do we calculate the partial pressure?
• Consider the ratio of $P_{\text{total}}$ to $P(\text{O}_2)$:

$$\frac{P_{\text{O}_2}}{P_{\text{total}}} = \frac{n_{\text{O}_2}RT/V}{n_{\text{total}}RT/V} = \frac{n_{\text{O}_2}}{n_{\text{total}}} = \chi_{\text{O}_2}$$

$$P_{\text{O}_2} = \frac{n_{\text{O}_2}}{n_{\text{total}}}P_{\text{total}} = \chi_{\text{O}_2}P_{\text{total}}$$

• $\chi_i$ is called the mole fraction of component i.
• $\chi$: Greek letter chi, pronounced “ki” rhymes with pi
• The pressure fraction is equal to the mole fraction.

Deep-sea diving vessels:

Oxygen and helium
TABLE 10.5 Vapor Pressure of Water at Different Temperatures

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$P_{\text{water}}$ (mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.6</td>
</tr>
<tr>
<td>20</td>
<td>17.5</td>
</tr>
<tr>
<td>21</td>
<td>18.6</td>
</tr>
<tr>
<td>22</td>
<td>19.8</td>
</tr>
<tr>
<td>23</td>
<td>21.1</td>
</tr>
<tr>
<td>24</td>
<td>22.4</td>
</tr>
<tr>
<td>25</td>
<td>23.8</td>
</tr>
<tr>
<td>30</td>
<td>31.8</td>
</tr>
<tr>
<td>40</td>
<td>55.3</td>
</tr>
<tr>
<td>50</td>
<td>92.5</td>
</tr>
<tr>
<td>100</td>
<td>760.0</td>
</tr>
</tbody>
</table>

Collecting a Gas over Water

1. Water levels inside and outside the test tube are the same to equalize pressure.

2. $P_{\text{total}} = P_{\text{gas}} + P_{\text{H}_2\text{O}}$
Example: A student generates oxygen gas and collects it over water. If the volume of the gas is 245 mL and the barometric pressure is 756 torr at 25°C, what is the volume of the “dry” oxygen gas at STP?
(P_{water} = 23.8 torr at 25°C)

\[ \text{P}_{O_2} = \text{P}_{bar} - \text{P}_{water} = (756 \text{ torr} - 23.8 \text{ torr}) = 732 \text{ torr} \]

\[ \frac{V_1 \cdot P_1}{T_1} = \frac{V_2 \cdot P_2}{T_2} \]

\[ V_2 = \frac{(V_1 \cdot P_1 \cdot T_2)}{(T_1 \cdot P_2)} \]

\[ = \frac{(245 \text{ mL})(732 \text{ torr})(273 \text{ K})}{(298 \text{ K})(760 \text{ torr})} \]

\[ = 217 \text{ mL} \]
Real Gases

- have a finite volume at absolute zero
- have attractive forces between gas particles.
- when molecules are crowded together at high pressures, impact of a given molecule with the wall is lessened. Thus, pressure is less than that of ideal gas because of rate of collisions is less.
- free, unoccupied space in which molecules can move is smaller than the container volume
- Temperature: cooling gas deprives molecules of energy needed to overcome mutual attraction.

Van der Waals Equation

\[(P + a/V^2)(V - b) = nRT\]

where \(a\) → attractive forces
\(b\) → residual volume

**First term:** attractive forces of between pairs of molecules increase as the square of the molecules per unit volume.

Magnitude of ‘a’ reflects how strongly the gas molecules attract each other.

**Second term:** accounts for finite volume occupied by gas molecules.
TABLE 10.6 Van der Waals Constants for Some Common Gases

<table>
<thead>
<tr>
<th>Gas</th>
<th>$a$ (L$^2$ atm/mol$^2$)</th>
<th>$b$ (L/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.054</td>
<td>0.0237</td>
</tr>
<tr>
<td>Ne</td>
<td>0.211</td>
<td>0.0171</td>
</tr>
<tr>
<td>Ar</td>
<td>1.35</td>
<td>0.0322</td>
</tr>
<tr>
<td>H$ _2$</td>
<td>0.244</td>
<td>0.0266</td>
</tr>
<tr>
<td>N$ _2$</td>
<td>1.39</td>
<td>0.0391</td>
</tr>
<tr>
<td>O$ _2$</td>
<td>1.36</td>
<td>0.0318</td>
</tr>
<tr>
<td>Cl$ _2$</td>
<td>6.49</td>
<td>0.0562</td>
</tr>
<tr>
<td>CO$ _2$</td>
<td>3.59</td>
<td>0.0427</td>
</tr>
<tr>
<td>CH$ _4$</td>
<td>2.25</td>
<td>0.0428</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>4.17</td>
<td>0.0371</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>5.46</td>
<td>0.0305</td>
</tr>
</tbody>
</table>

For all pressures the quotient $PV/nRT$ for an ideal gas is 1.
A pea in a basketball corresponds roughly to the relative volume that gas molecules have to move about in without striking another gas molecule at STP.

When the pressure is increased to 1000 atm, the relative volumes are like a pea in a ping-pong ball.

A gas molecule strikes the walls of a container with less force due to the attractive forces between it and its neighbors.