Unit 6
Ideal Gases
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1 Measurements on Gases

Let’s look at a certain amount of gas, e.g. trapped inside a balloon. To completely describe the state of this gas one has to specify the following quantities:

**Volume**
Symbol: \( V \)
Units: L \( 1 \text{ L} = 10^{-3} \text{ m}^3 \)

(remember that L is not a SI unit)

**Temperature**
Symbol: \( T \)
Units: K (“Kelvin”). The Kelvin scale is the “absolute temperature” scale.
To convert ° C to K we simply add 273
(actually it is 273.15, but in most cases “273” will do)

Example: \( 25° \text{ C} = (25 + 273) \text{ K} = 298 \text{ K} \)

**Pressure**
Symbol: \( p \)
Units: force per area \( 1\text{ Pa} \) (Pascal) = \( 1 \text{ N/m}^2 \)

\( 1000 \text{ Pa} = 1 \text{ kPa} \)
Other units are still used for pressure:
- psi = pound per square inch (we are not going to use that)
- \( 10^5 \text{ Pa} = 1 \text{ bar} \)
A *mercury barometer* can be used for measuring gas pressure

“Normal pressure” corresponds to 101.3 kPa = **760 mm Hg** ( =1 atm).

The Hg level will be lower when you move this device from the basement to the third floor, or when a rainstorm is moving in (why?)
2. *Number of Moles*

With gases, as with any other substances we can use the relationship

\[ m = MM \times n \]

to convert mass \((m)\) to number of moles \((n)\), if we know the molar mass \((MM)\).

Example: How many moles of \(N_2\) molecules are there in 2.50 g?

\[ m = 2.50\text{g} \]

\[ \text{MM} = 28\text{ g/mol} \]

or

\[ 2.50\text{g} = 28\text{ g/mol} \times n \]

\[ n = \frac{(2.50\text{g})}{(28\text{g/mol})} = .089\text{ mol} \]
Calculations involving gases can be confusing because of the different units that are sometimes used for the same quantity.

That means: *before* you do any calculations

- Convert the volume to $L$
- Convert the pressure to $kPa$
- Convert the temperature to $K$
- Convert the “amount” of material to moles

… and you’ll be OK 😊
3 The Ideal Gas Law
Pressure, temperature, volume, and number of moles are related by the ideal gas law:

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

where \( R = 8.31 \text{ L kPa mol}^{-1} \text{ K}^{-1} \) is a constant

If you use this value of \( R \) in calculations, \( V \) has to be in L, \( P \) has to be in kPa !!!!

(In SI units: \( R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1} \))

Although this law only applies to “ideal” gases (meaning that the molecules do not interact with each other, individual gas molecules have zero volume)

it describes the behavior of real gases (He, O\(_2\), N\(_2\), … remarkably well).

Remember: \( n \) is the number of gas molecules (not gas atoms !!!!), i.e.

- for 1 mol He \( n = 1 \)
- for 1 mol N\(_2\) \( n = 1 \)
What does the ideal gas law tell us? Let’s try this for V

- The volume is proportional to the number of moles (for fixed $T$, fixed $p$):

$$V = \frac{nRT}{P}$$

- The volume is proportional to the temperature (for fixed $n$, fixed $p$):

$$V = \frac{nRT}{P}$$

- The volume is inversely proportional to the pressure (for fixed $n$, fixed $T$)

$$V = \frac{nRT}{P}$$
Example: How much volume is occupied by one mole of gas at *standard temperature and pressure* ("STP"), i.e. 0° C and 101.3 kPa (1 atm)?

\[ V = \frac{nRT}{P} \]

\[ = (1.0 \times 8.31 \text{ L kPa mol}^{-1} \text{ K}^{-1} \times 273 \text{ K})/(101.3 \text{ kPa}) \]

\[ = 22.4 \text{ L} \]

This result does not depend on the nature of the gas! 1 mol He occupies the same volume as 1 mol Cl$_2$ …
Postulates of the Ideal Gas Law:

1. Gases are composed of molecules in rapid random motion. The kinetic energy of the gas molecules depends on the temperature, pressure results from collision of the gas molecules with the container walls.

2. The gas molecules do not exert any forces on each other.

3. The volume of the gas molecules themselves are negligible compared to the volume of the container.

These postulates work surprisingly well. Molecules do exert attractive forces on each other but the attraction may be ignored when the molecules are far apart (low pressure, or high temperature); in addition, the molecules do have a volume of their own but this volume may also be neglected at low pressure.

Under non-ideal conditions (high pressure and/or low temperature) a refinement of the ideal gas law is used, usually the Van Der Waals equation.
Dec. 2004 exam question:

19. A 25.0 L cylinder of N₂(g) has an internal pressure of 5.0 × 10³ kPa at 20°C. A valve is opened and the gas is released until the internal pressure become 2.0 × 10³ kPa. The number of moles of nitrogen gas that escapes at constant temperature is

| A) 20.5 | B) 11.0 | C) 7.32 | D) 30.8 | E) 18.3 |

Find # moles of gas originally present:

\[ n = \frac{PV}{RT} = \frac{(5000 \times 25)}{(8.31 \times 293)} = 51.3 \]

# of moles after release:

\[ n = \frac{(2000 \times 25)}{(8.31 \times 293)} = 20.5 \]

Moles released = 51.3 – 20.5 = 30.
4. More Gas Law Calculations

Final and Initial State Problems

A gas often undergoes a change from an initial to a final state.

Example: Consider a sample of gas at 25° C and 101.3 kPa (1.000 atm) [initial state, state_1]. What is the pressure if the gas is heated to 100° C at constant volume [final state, state_2]?

Using the ideal gas law, and remembering that \( n = \text{const} \), \( V = \text{const} \) (and, of course \( R = \text{const} \)), we find that

Initial state: \( P_1V = nRT_1 \)
Final state: \( P_2V = nRT_2 \)

If \( n = \text{const} \), but \( p, V, T \) change you have

\[
P_1V_1 = nRT_1 \quad \quad P_2V_2 = nRT_2
\]

such that \( \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \)  
(remember this for the gases prelab)

Here: \( P_1 = 101.3 \text{ kPa} \), \( P_2 = x \), \( T_1 = 298 \text{ K} \), \( T_2 = 373 \text{ K} \), \( V_1 = V_2 \)  
So that:

\[
\frac{(101.2 \text{ kPa})/298}{(373/298)} = \frac{x \text{ kPa}}{373/298}
\]

\( x = P_2 = 101.2 \times \frac{373}{298} \approx 126.7 \text{ kPa} \)
Molar Mass and Density
The ideal gas law offers a simple approach to the experimental determination of the molar mass of a gas. This method can also be applied to volatile liquids (i.e. liquids that evaporate easily, e.g. “nail polish remover” [= acetone]).

A simple derivation shows how this might be done:

\[ PV = nRT \]

\[ N = \frac{\text{mass}}{\text{MM}} \text{ or } PV = \left(\frac{\text{mass}}{\text{MM}}\right)RT \]

or: \[ P \times \text{MM} = \left(\frac{\text{mass}}{V}\right) \times RT \]

but: \[ \frac{\text{mass}}{V} = \text{density} \ (d) \]

so that: \[ \text{MM} = \frac{\left(dRT\right)}{P} \]
Example:
A sample of liquid acetone is placed in a 3.00 L flask and vaporized by heating to 95° C at 103.3 kPa (1.02 atm). The vapor filling the flask at this temperature and pressure weighs 5.87 g (you can assume that there is no air left in the flask, i.e. it contains only acetone vapor).

a) What is the density of acetone vapor under these conditions?
b) Calculate the molar mass of acetone.

a) \( d = \frac{\text{mass}}{\text{vol}} = \frac{5.87\, \text{g}}{3.00\, \text{L}} = 1.96\, \text{g/L} \)

b) \( \text{MM} = \frac{dRT}{P} = \left(1.96\, \text{g/L} \times 8.31\, \text{L kPa mol}^{-1}\, \text{K}^{-1} \times 368\, \text{K}\right)/ (103.3\, \text{kPa}) \)

\( \text{MM} = 58\, \text{g/mol} \)

How does this compare to the expected molar mass of acetone [molecular formula CH\(_3\)-CO-CH\(_3\) ] ?
Same
Dec 2004 exam question:

20. The minor planet Xebon has an atmosphere composed solely of xenon, Xe. If, at the surface the pressure were 1.01 kPa and the temperature 20°C, the density (g L⁻¹) of the atmosphere at the surface would be

A) 0.54  B) 0.80  C) 1.31  D) 8.0 x 10²  E) 5.4 x 10⁻²

\[
\text{MM} = \frac{\text{dRT}}{P} = 131.3 \text{g/mol} = \left(\text{d} \times 8.31 \text{ L kPa mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}\right)/1.01 \text{ kPa}
\]

\[
d = 5.4 \times 10^{-2} \text{g/L}
\]
... and another one

21. The density of liquid bromine, Br₂, at its boiling point of 58.7°C is 3.12 g mL⁻¹. By what factor would a sample of bromine expand if it evaporated to form a gas at 58.7°C and 101.3 kPa?

A) 266  B) 340  C) 170  D) 85  E) 532

We want
We can start with any arbitrary mass of Br₂(l), 3.12 g looks like a good choice because we know the volume of this mass = 1 mL = 0.001 L

Now all we need to know is what volume this much bromine as a gas would occupy under the conditions given. Since it is a gas,

PV = nRT

P = 1 atm = 101.3 kPa (normal boiling point)

V = Volume Br₂(g)

n = mass/MM = 3.12g/159.8 g/mol  recall MM for Br₂ = 159.8g

= .0195 mol

R = 8.31 L kPa mol⁻¹ K⁻¹

T = 58.7 + 273 = 331.7 K

Volume Br₂(g) = (0.0195 mol x 8.31 L kPa mol⁻¹ K⁻¹ x 331.7 K)/ 101.3 kPa

= 0.530 L

Expansion factor = (Volume Br₂(g))/ (Volume Br₂(l)) = 0.530 L/0.001 L = 530
5. Stoichiometry of Gaseous Reactions

We already know how to relate moles of substance to grams of substance (using \( m = MM \times n \)). For gas reactions we can now also include volume and pressure.

The following Dec 2004 exam question.

22. Pentane, \( C_5H_{12} \), burns in oxygen to form carbon dioxide and water. The volume (L) of \( O_2(g) \) at 100 kPa and 20°C that is required to react completely with 5.00 g of \( C_5H_{12} \) is

A) 0.115  B) 67.5  C) 0.921  D) \( 8.78 \times 10^{-3} \)  E) 13.5

The balanced equation is:

\[
C_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6 H_2O
\]

We need 8 moles \( O_2 \) for each mole \( C_5H_{12} \)

We have \( 5/72 = 0.0694 \) moles \( C_5H_{12} \)

Need \( 8 \times 0.0694 = 0.556 \) moles \( O_2 \)

Volume \( O_2 \) required = \( nRT/P = (0.556 \times 8.31 \text{ L kPa mol}^{-1} \text{K}^{-1} \times 293 \text{ K})/100 \text{ kPa} \)

= 13.5 L
Gay-Lussac discovered the law of combining volumes: The volume ratio of any two gases in a reaction at constant temperature and pressure is the same as the reacting mole ratio.

Example:

Synthesis of ammonia

\[ \text{N}_2 \ (g) \ + \ 3 \text{H}_2 \ (g) \ \rightarrow \ 2 \text{NH}_3 \ (g) \]

1 molecule of \( \text{N}_2 \) and 3 molecules of \( \text{H}_2 \) will produce 2 molecules of \( \text{NH}_3 \)

1 mole of \( \text{N}_2 \) and 3 moles of \( \text{H}_2 \) will produce 2 moles of \( \text{NH}_3 \)

and …

1 L of \( \text{N}_2 \) and 3 L of \( \text{H}_2 \) will produce 2 L of \( \text{NH}_3 \)

10 m\(^3\) of \( \text{N}_2 \) and 30 m\(^3\) of \( \text{H}_2 \) will produce 20 m\(^3\) of \( \text{NH}_3 \)

This works, because \( V = (RT/p) \times n \)

The volume is proportional to the number of moles!

Analogously, this works with partial pressures
Feb 2005 exam question:

2. For the gas-phase combustion of the compound $C_xH_yO_z$, the following volume relationships were found at constant temperature and pressure:

$$C_xH_yO_z(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$$

2 vols 5 vols 4 vols 4 vols

From these data, the molecular formula of $C_xH_yO_z$ is:

A) $C_2H_6O$  B) $CH_4O$  C) $CH_4O_2$  D) $C_2H_4O$  E) $C_2H_4O_2$

Since volumes are interchangeable with moles the equation is:

$$2 C_xH_yO_z + 5O_2 \rightarrow 4CO_2 + 4H_2O$$

Now moles C in $2 C_xH_yO_z = $ moles C in $4 CO_2$

So $2x = 4$  $x= 2$ Formula so far = $C_2H_yO_z$

And:

Moles H in $2 C_2H_yO_z = $ moles H in $4H_2O$

So: $2 y = 4 x2 y= 4$ Formula so far = $C_2H_4O_z$

Now moles O on reactant side = moles O on product side:

$$2z + 10 = 12$$

$z = 1$ Formula is: $C_2H_4O$
6. Gas Mixtures: Partial Pressures and Mole Fractions

The ideal gas law applies to all gases, therefore it should also apply to gas mixtures (e.g. air).

Consider a mixture of two gases at constant volume and temperature (moles gas A = \( n_A \), moles gas B = \( n_B \)), the total pressure is given by

\[
p_{tot} = n_{tot} \times \frac{RT}{V} = (n_A + n_B) \times \frac{RT}{V} \\
= n_A \times \frac{RT}{V} + n_B \times \frac{RT}{V} \\
= p_A + p_B
\]

\( p_A \) and \( p_B \) are the same pressures that gas A and gas B would exert if they were alone. They are referred to as partial pressures.

The total pressure is the sum of the partial pressures of all gases

In this case:

\[
p_{tot} = p_A + p_B
\]

The partial pressures are simply calculated from the ideal gas law:

\[
p_A = n_A \frac{RT}{V} \\
p_B = n_B \frac{RT}{V}
\]
If there are more than two gases:

\[ p_{\text{tot}} = p_A + p_B + p_C + \ldots \]

This is known as *Daltons Law of Partial Pressures*: “The total pressure of a gas mixture is the sum of the partial pressures of the components of the mixture.”

And in a gas mixture:

\[ P_A = X_A P_T \]

\[ X_A = \text{mole fraction of gas A} = \frac{\text{moles a}}{\text{total moles gas in mixture}} \]
Dec 2004 exam question:

23. A steel flask of volume 23.0 L contains a gas mixture which consists of 0.475 g of H₂ and an unknown amount of helium. If the total pressure of the mixture is 100.0 kPa at a temperature of 29°C, the partial pressure (kPa) of He in the mixture is

A) 25.7  B) 81.9  C) 59.0  D) 74.3  E) 41.0

\[ P_T = P_{He} + P_{H2} = 100.0 \text{ kPa} \]

\[ P_{H2} = X_{H2}P_T \]

\[ P_{He} = X_{He}P_T \]

The total # of moles of gas in the system may be found using PV = nRT

\[ n = \frac{RT}{PV} = \frac{8.31 \times 302}{100 \times 23} = 1.09 \]

moles H₂ = mass/molar mass = \( \frac{0.475}{2} = 0.2875 \)

moles He = moles total – moles H₂ = 1.09 – 0.2875 = 0.8

\[ P_{He} = X_{He}P_T = \left( \frac{\text{moles He}}{\text{moles He} + \text{moles H}_2} \right) \times P_T \]

\[ = \left( \frac{0.8}{0.8 + 0.2875} \right) \times 100 = 73.4 \]
Dec 2004 exam question:

24. A mixture of C₂H₂ and excess H₂ in a one-litre vessel exerts a pressure of 52.0 kPa. After a spark initiates the reaction

\[ \text{C}_2\text{H}_2(g) + 2 \text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g) \]

and the products cool to the the same temperature as that of the initial mixture, the final pressure is 34.0 kPa. The partial pressure (kPa) of C₂H₂(g) in the mixture of C₂H₂ and H₂ was therefore

A) 36.0  B) 9.0  C) 4.5  D) 6.0  E) 18.0

Before reaction:

\[ P_{T(\text{initial})} = P_{\text{C}_2\text{H}_2(\text{initial})} + P_{\text{H}_2(\text{initial})} = 52.0 \text{ kPa} \]

After reaction:

\[ P_{T(\text{final})} = P_{\text{C}_2\text{H}_6(\text{final})} + P_{\text{H}_2(\text{final})} = 34.0 \text{ kPa} \]

Now since 1 mole C₂H₂ yields 1 mole C₂H₆ and H₂ is in excess, after reaction \( P_{\text{C}_2\text{H}_2(\text{initial})} = P_{\text{C}_2\text{H}_6(\text{final})}, \) so that:

\[ P_{T(\text{initial})} - P_{T(\text{final})} = P_{\text{H}_2(\text{initial})} - P_{\text{H}_2(\text{final})} = 52 - 34 = 18 \text{ kPa} \]

\[ = \Delta P_{\text{H}_2} \]

Now: 2 moles H₂ react with 1 mol C₂H₂ or \( \Delta P_{\text{H}_2}/2 = P_{\text{C}_2\text{H}_2(\text{initial})}. \)

\[ P_{\text{C}_2\text{H}_2(\text{initial})} = 18/2 = 9 \text{ kPa} \]
7. Wet Gases, Partial Pressure of Water

Consider the following arrangement: A closed container contains some liquid water and a gas (say N$_2$).

**Q.** What is the total pressure of the gas?

**A.** It is the partial pressure of the N$_2$, plus that of the water vapor.

\[ p_{tot} = p_{N2} + p_{H2O} \]

The partial pressure of the water vapor is equal to the so-called *vapor pressure* of liquid water. It has a fixed value at a given temperature.
The vapor pressure of water is independent of the amount of liquid water (… as long as there is any liquid water)!

Vapor pressure of water as a function of temperature. (taken from lab manual)

An example of an experiment where this is important is the following: Zn + 2H\(^+\) → Zn\(^{2+}\) + H\(_2\). The H\(_2\) gas is collected by displacing water …

The total pressure of the collected gas is \(p_{H_2} + p_{H_2O}\).

Example: Electrolysis of water

Hydrogen gas is prepared by electrolyzing water at 25° C. 152 mL of hydrogen are collected at a total pressure of 101 kPa.

What is the partial pressure of hydrogen under these conditions?
\[ p_{\text{tot}} = p_{N_2} + p_{H_2O} = 101 \text{ kPa} = p_{N_2} + 3.17 \text{ kPa} \]

(from table)

\[ p_{N_2} = 97.83 \text{ kPa} \]

How many moles of hydrogen were collected?

Use: \( PV = nRT \)

\[
97.83 \text{ kPa} \times 0.154 \text{ L} = n \times 8.31 \text{ L kPa mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}
\]

\[ n = 6.1 \times 10^{-3} \]
5. A sample of $O_2(g)$ is collected over water at 50°C and 94.6 kPa. The volume collected over the water is 2.00 L. How many grams of $O_2(g)$ are obtained?

A) 2.25  B) 0.293  C) 1.96  D) 2.40  E) 0.980

From the data page: vapor pressure of water at 50°C = 12.3 kPa

\[ P_{O_2} = P_T - P_{O_2} = 94.6 - 12.3 = 82.3 \text{ kPa} \]

Now use \(PV = nRT\)

\[ n_{O_2} = \frac{(82.3 \text{ kPa} \times 2 \text{ L})}{(8.31 \text{ L kPa mol}^{-1} \text{ K}^{-1} \times 323 \text{ K})} = 0.061 \text{ mol} \]

Mass $O_2 = \text{moles} \times \text{MM} = 0.061 \times 32 = 1.96 \text{ g}$
Example:

1 mole of methane is heated in the presence of 4 moles of oxygen. The following reaction occurs:

\[
\text{CH}_4(g) + 2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(g)
\]

what are the mole fractions of \( \text{O}_2 \), \( \text{CO}_2 \), and \( \text{H}_2\text{O} \) in the resulting mixture?

1 mol of \( \text{CO}_2(g) \) is produced.

2 mol of \( \text{H}_2\text{O}(g) \) are produced.

2 mol of \( \text{O}_2 \) remain unreacted.

All the \( \text{CH}_4(g) \) is consumed.

\[
X_{\text{CO}_2} = 1/(1 + 2 + 2) = 0.2
\]

\[
X_{\text{H}_2\text{O}} = X_{\text{O}_2} = 2/(1 + 2 + 2) = 0.4
\]

If the total pressure of the resulting gas mixture is 126 kPa, what are the partial pressures?

\[
P_{\text{O}_2} = X_{\text{O}_2} \times P_T = 0.4 \times 126 \text{ kPa} = P_{\text{H}_2\text{O}} = 50.4 \text{ kPa}
\]

\[
P_{\text{CO}_2} = X_{\text{CO}_2} \times P_T = 0.2 \times 126 = 25.2 \text{ kPa}
\]