Chemistry 115

Chapter 11 – Review

Chapter 11 (sections 1 to 4)

- Pressure
  - Definition, units
- Gas Laws from Experiment
  - Boyle's Law, Charles' Law, the General Gas Law and Avogadro's Hypothesis
- The Ideal Gas Law
  - Definition, the Gas Constant, STP and Density
- Gas Laws and Chemical Reactions

Pressure

- **Definition:** Pressure (p) equals force (F) per unit area (A):

$$P = \frac{F}{A}$$

- **Units:** There are many different units and scales of pressure in common use.
    - The SI units of force and area are Newtons (N) and square meters (m^2), respectively
    - The SI unit for pressure is therefore N/m^2, which is also known as a Pascal (Pa)

Pressure

- **Units:** 1 Pascal is a relatively small value of pressure, so the kilopascal (kPa) is often more useful when considering gas pressure.

- Other common units of pressure used for gases include:
  - Standard atmosphere (atm): 101.325 kPa = 1 atm
  - Millimeters of mercury (mm Hg): 760 mm Hg = 1 atm
  - Bar (bar): 1.01325 bar = 1 atm

Pressure

- **Converting Pressure Units:** Use dimensional analysis, as described in Chapter 1 (pages 38 and 39)

- Example 1: Converting 798 mm Hg into atm

$$798\ \cancel{mm\ Hg} \times \frac{1\ atm}{760\ \cancel{mm\ Hg}} = 1.05\ atm$$

Pressure

- **Converting Pressure Units:** Use dimensional analysis, as described in Chapter 1 (pages 38 and 39)

- Example 2: Converting 0.98 atm into bar

$$0.98\ \cancel{atm} \times \frac{1.01325\ bar}{1\ \cancel{atm}} = 0.99\ bar$$

Pressure

- **Converting Pressure Units:** Use dimensional analysis, as described in Chapter 1 (pages 38 and 39)

- Example 3: Converting 1.40 atm into kPa

$$1.40\ \cancel{atm} \times \frac{101.325\ kPa}{1\ \cancel{atm}} = 141.855\ kPa$$

Gas Laws from Experiment

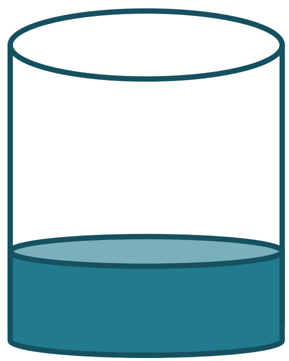
- Before the development of modern physics, people formulated laws to describe the behaviour of gases based on experiments and on their observations of the world around them.

Gas Laws from Experiment

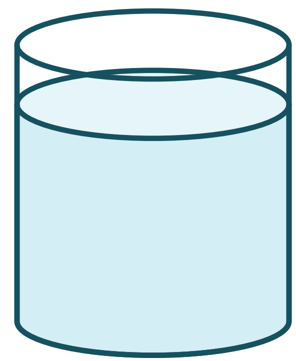
- For example, Robert Boyle (1627–1691) observed a relationship between the pressure exerted by a fixed quantity of gas, and the volume that it occupied.
  - When he compressed the gas (squashed it into a smaller volume), the pressure increased
  - When he allowed the gas to expand to fill a larger volume, the pressure decreased

Gas Laws from Experiment

- **Boyle’s Law:** Illustration



Small volume, V
Large pressure, P



Large volume, V
Small pressure, P

- For fixed values of temperature (T) and quantity of gas (number of moles, n)

Gas Laws from Experiment

- **Boyle's Law:** Mathematical Expression

$$P \propto \frac{1}{V} \quad \text{or} \quad \mathrm{V} \propto \frac{1}{P}$$

- And, following from this:

$$P_1V_1 = P_2V_2$$

- For fixed values of temperature (T) and quantity of gas (number of moles, n)

Gas Laws from Experiment

- Following on from the work by Robert Boyle linking pressure and volume, in the 18th century, Jacques Charles (1746–1823), formulated the relationship between the temperature and the volume of a gas

  - When he reduced the temperature (cooled) a fixed quantity of gas at a fixed pressure, the volume decreased

  - When he increased the temperature (heated) a fixed quantity of gas at a fixed pressure, the volume increased

Gas Laws from Experiment

- **Charles' Law:** Illustration

(a) (b) (c)

Gas Laws from Experiment

- **Charles' Law:** Mathematical Expression

$$V \propto T$$

- And, following from this:

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

- For fixed values of pressure (P) and quantity of gas (number of moles, n)

Gas Laws from Experiment – Units

- **Important:** Temperature must always be in Kelvin.

Gas Laws from Experiment

- **The General Gas Law:** Combines Boyle's and Charles' Laws into one equation, which can be used for situations in which the quantity of gas (n) does not change

$$P_1V_1 = P_2V_2 \quad + \quad \frac{V_1}{T_1} = \frac{V_2}{T_2} \quad = \quad \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

- The General Gas Law is also called the Combined Gas Law

Gas Laws from Experiment

- **The General Gas Law**: Example
- What is the pressure in my car tyre at midday, when the temperature is 37.0°C and the volume of the tyre is 51.7 L, if the pressure was 3.20 atm and the volume was 49.4 L at dawn, when the temperature was only 25.0°C?

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Gas Laws from Experiment

- **The General Gas Law**: Example

- What is the pressure in my car tyre at midday, when the temperature is 37.0°C and the volume of the tyre is 51.7 L, if the pressure was 3.20 atm and the volume was 49.4 L at dawn, when the temperature was only 25.0°C?

- First, identify the known and unknown values:

  - In the morning, $P_1 = 3.20$ atm, $V_1 = 49.4$ L and $T_1 = 25.0$°C

  - At midday, $V_2 = 51.7$ L, $T_2 = 37.0$°C and P_2 is the unknown

Gas Laws from Experiment

- **The General Gas Law:** Example

- What is the pressure in my car tyre at midday, when the temperature is 37.0°C and the volume of the tyre is 51.7 L, if the pressure was 3.20 atm and the volume was 49.4 L at dawn, when the temperature was only 25.0°C?

- Convert the temperatures into Kelvin:
  - $T_1 = 25.0°C$ $\quad$ $T_1 = 298K$
  - $T_2 = 37.0°C$ $\quad$ $T_2 = 310K$

Gas Laws from Experiment

- **The General Gas Law:** Example

- What is the pressure in my car tyre at midday, when the temperature is 37.0°C and the volume of the tyre is 51.7 L, if the pressure was 3.20 atm and the volume was 49.4 L at dawn, when the temperature was only 25.0°C?

- Then, put the values into the equation to find the unknown:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \therefore \quad \frac{3.20 \times 49.4}{298} = \frac{P_2 \times 51.7}{310}$$

  - **Note: omitting units here to save space

Gas Laws from Experiment

- **The General Gas Law**: Example
- What is the pressure in my car tyre at midday, when the temperature is 37.0°C and the volume of the tyre is 51.7 L, if the pressure was 3.20 atm and the volume was 49.4 L at dawn, when the temperature was only 25.0°C?
- And finally, perform the calculation to find P_2:

$$P_2 = \frac{3.20 \times 49.4 \times 310}{298 \times 51.7} = 3.18\, atm$$

Gas Laws from Experiment

- Boyle's Law, Charles' Law and the General (Combined) Gas Law only apply for fixed quantities of gas.

- But how can we relate the volume, pressure or temperature to the quantity of gas, so that we can calculate the properties of gases for which the quantity is a variable too?

Gas Laws from Experiment

- **Avogadro's Hypothesis** links volume (V) to the quantity of gas (number of moles, n)

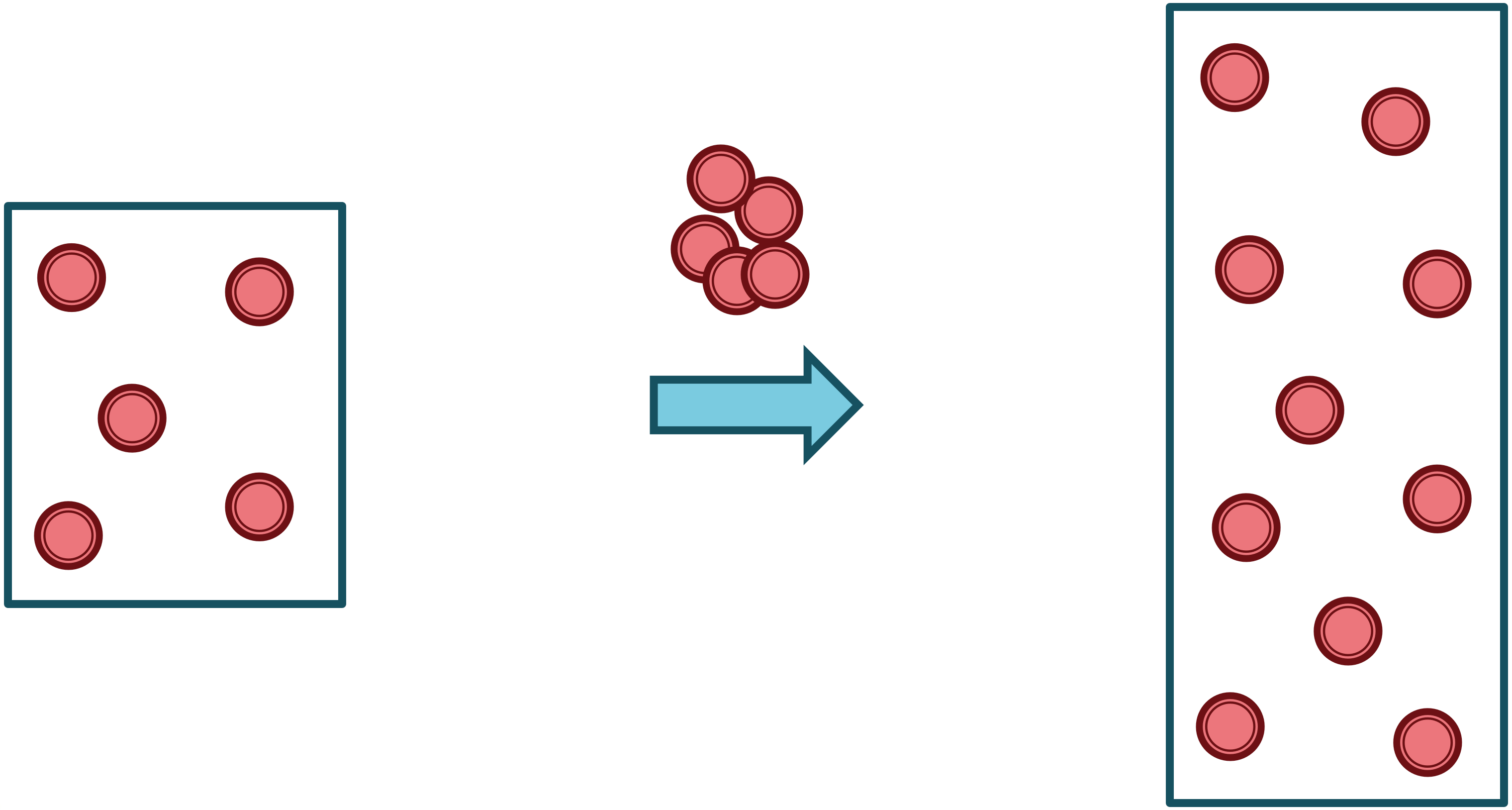
- (The same Avogadro as the Avogadro number)

  - The volume of the gas is directly proportional to the number of gas molecules, at fixed temperature and pressure

$$V \propto n$$

Gas Laws from Experiment

- **Avogadro's Hypothesis:** Illustration



Gas Laws from Experiment

- **Avogadro's Hypothesis**: Example (q 15, page 546)

$$2\,NO\,(g) + O_2\,(g) \rightarrow 2\,NO_2\,(g)$$

- If we have 150 ml of NO, what volume of O_2 is needed, and what volume of NO_2 is produced?
- Assuming constant temperature (*T*) and pressure (*P*)

Gas Laws

- **Variables:** The four variables we need to consider in problems concerning gases are:

Variable	Symbol	Unit(s)
Temperature	T	K, °C, °F
Pressure	P	kPa, atm, bar, mm Hg
Volume	V	L, ml, cm^3
Quantity	n	Mol, or occasionally g

Gas Laws – Summary

- **Variables**: Boyle's Law, Charles' Law, the General Gas Law and Avogadro's Hypothesis each contain 2 or 3 of a total of 4 variables.
- The variables that are not included in the equation must be fixed (constant) for the equation to work in a particular case

$$P_1V_1 = P_2V_2$$

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

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$V \propto n$$

The Ideal Gas Law

- The Ideal Gas Law is an equation that combines the previous equations and that links all four variables describing gases – temperature, pressure, volume and quantity

$$V \propto \frac{1}{P} \qquad V \propto T \qquad V \propto n$$

- To make this combination and give the ideal gas equation, a proportionality constant, R, is introduced:

$$V \propto \frac{nT}{P} \quad \Rightarrow \quad V = R\,\frac{nT}{P}$$

The Ideal Gas Law

- **Note:** the ideal gas equation can be expressed in more than one way:

$$PV = nRT$$

$$V = R\left(\frac{nT}{P}\right)$$

- These expressions have the same meaning and validity; they are simply rearrangements

The Gas Constant, R

- The proportionality constant, R, in the ideal gas equation is known as the gas constant

$$PV = nRT$$

- R is a universal constant, which can be used to describe any gas that obeys the ideal gas law

The Gas Constant, R

- R can be determined experimentally by carefully measuring P, V and T for a known quantity of gas:

$$PV = nRT$$

- **Example:** At Standard Temperature and Pressure (STP)

  - Pressure = 1 atm
  - Temperature = 273.15 K
  - Quantity = 1 mol
  - Volume = 22.414 L (Standard molar volume)

  - R is determined to be 0.082057 L atm K^{-1} mol^{-1}

Ideal Gas Law and Density

- We can combine the definition of density with the ideal gas equation to give us a formula that expresses the density of any gas in terms of its pressure, temperature and molar weight:

$$d = \frac{mass}{V} \qquad n = \frac{mass}{M} \qquad PV = nRT$$

- M is the molar weight of the gas in grams

Ideal Gas Law and Density

- Substituting the definition of n, and rearranging the ideal gas equation gives:

$$d = \frac{mass}{V} = \frac{PM}{RT}$$

Ideal Gas Law and Density

- **Example:** Why do helium balloons float? Can we give a quantitative explanation, based on the ideal gas laws?

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Ideal Gas Law and Density

- **Example:** Why do helium balloons float?
- **Strategy:**
  - What is the density of helium at STP?
  - What is the density of air at STP?

Ideal Gas Law and Density

- **Example:** Why do helium balloons float?

- **Strategy:**
  - What is the density of helium at STP?
  - STP: 1 atm pressure and 273.15 K, R is 0.082057 L atm K^{-1} mol^{-1} and the molar weight of He is 4.0026 g.

$$d = \frac{PM}{RT} = \frac{1.0 \times 4.0026}{0.082057 \times 273.15} = 0.18\ gL^{-1}$$

Ideal Gas Law and Density

- **Example:** Why do helium balloons float?

- **Strategy:**

  - What is the density of air at STP (assuming that air is 80% nitrogen and 20% oxygen by mass)?

  - First, calculate an average M for the sample using the relative abundance:

$$M = \frac{80}{100}(2 \times 14.007) + \frac{20}{100}(2 \times 15.999) = 28.8108\ g$$

Ideal Gas Law and Density

- **Example:** Why do helium balloons float?

- **Strategy:**

  - What is the density of air at STP (assuming that air is 80% nitrogen and 20% oxygen by mass)?

  - Then, use this value of M (28.8108g) to calculate the density of air at STP:

$$d = \frac{PM}{RT} = \frac{1.0 \times 28.8108}{0.082057 \times 273.15} = 1.3\ gL^{-1}$$

Ideal Gas Law and Density

- **Example:** Why do helium balloons float?
- **Conclusion:**
  - The density of helium at STP is 0.18 gL^{-1}, and the density of air at STP is 1.3 gL^{-1}
  - Therefore air is 'heavier' than helium, per unit volume
  - Incidentally, our 'approximate' calculation of the density of air is very close to the real value, of 1.2gL^{-1}.

Gas Laws and Chemical Reactions

- **Stoichiometry:** the calculation of quantities, and especially the ratio of quantities, of elements and compounds in a chemical reaction

$$2\,H_2 + \;O_2 \;\rightarrow 2\,H_2O$$

  - The ratio of the elements must be correct, to give the correct compound(s)
  - The overall reaction must be balanced – we do not create or destroy atoms in a chemical reaction

Gas Laws and Chemical Reactions

- **Stoichiometry**: the calculation of quantities, and especially the ratio of quantities, of elements and compounds in a chemical reaction

$$2\,H_2 + \;O_2 \;\rightarrow 2\,H_2O$$

- We will look at this concept in more detail when we cover Chapters 3 and 4.