Gases

- Petrucci, Harwood and Herring: Chapter 6

- We will be looking at Macroscopic and Microscopic properties:
  - Macroscopic
    - Properties of bulk gases
    - Observable
      - Pressure, volume, mass, temperature…
  - Microscopic
    - Properties at the molecular level
    - Not readily observable
      - Mass of molecules, molecular speed, energy, collision frequency

Macroscopic Properties

- Our aim is to look at the relationship between the macroscopic properties of a gas and end up with the gas laws

Pressure

- To contain a gas you must have a container capable of exerting a force on it (e.g. the walls of a balloon).
- This implies that the the gas is exerting a balancing force
- Normally we talk about the pressure (force/area) rather than force

Measuring Pressure

- The simplest way to measure gas pressure is to have it balance a liquid pressure.
- Therefore we need to quantify the liquid pressure

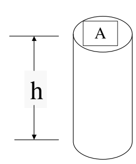
- Consider a cylinder of liquid with area A and height h
- The force exerted at the bottom of the cylinder is its weight

  $F = m.g$
- The pressure exerted is

  $P = F/A = m.g/A$
- The density of the liquid is

  $d=m/V$ and $m = d.V$ but $V=A.h$
- So

  $P = m.g/A = g.V.d/A = g.A.h.d/A = g.h.d$



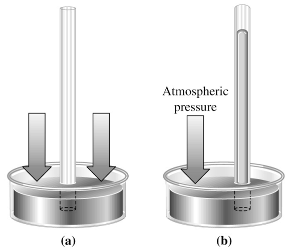
Barometer

To measure Atmospheric Pressure

On the left the tube is open

On the right the tube is closed and a liquid column is supported by the atmospheric pressure:

Air pressure equals the liquid pressure



Barometer (continued)

So for a barometer

P=g.h.d P=atmospheric pressure
h = height of liquid column
d = density of the liquid

Atmospheric Pressure

- By definition the average pressure at sea level will support a column of 760 mm of mercury. (760 torr)
- What is this in SI units?

P=g.h.d

$g = 9.81\ m.s^{-2}$, $h = 0.76\ m$,

$d_{Hg} = 13.6\ g.cm^{-3} = 13.6\ kg.L^{-1} = 13.6x10^{3}\ kg.m^{-3}$

$P = 9.81x0.76x13.6x10^{3} = 1.013x10^{5}\ Pa\ (N.m^{-2})$

If we made a barometer out of water, what would be the height of the water column if the pressure is 745 torr?

The problem calls for the relationship between P and h

P = g.h.d

$$P = \frac{745}{760} \times 1.013 \times 10^{5} \quad \text{Pa}$$

$$d = 1.00 \text{ g cm}^{-3} = 1.00 \times 10^{3} \text{ kg m}^{-3}$$

$$g = 9.81 \text{ m s}^{-2}$$

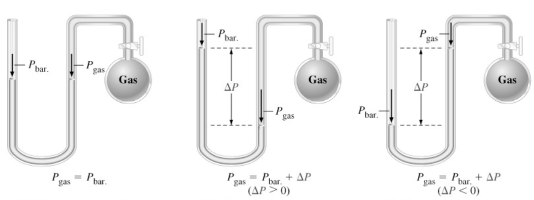
$$P = g.h.d$$

$$\frac{745}{760} \times 1.013 \times 10^{5} = 9.81 \times h \times 1.00 \times 10^{3} \quad \therefore h = 10.1 \text{ m}$$

Measuring Gas Pressures

Gas pressures can be measured with a manometer. This is similar to a barometer but measures pressure differences using a liquid.

When one side of the manometer is open to the atmosphere



(a) Gas pressure equal to barometric pressure **(b)** Gas pressure greater than barometric pressure **(c)** Gas pressure less than barometric pressure

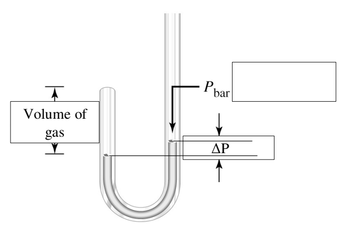
$$\Delta P = g.h.d$$

Gas Laws

- The aim is to determine the relationship between the gas observables (pressure, volume, mass, temperature).
- These were determined experimentally

Boyle's Law

- Boyle (~1622) kept the mass of gas and the temperature constant and studied the relationship between pressure and volume



Boyle's Law

- Boyle found that pressure and volume were inversely proportional. (double the pressure and the volume goes to one half).
- This is usually expressed as

$$P.V = \text{constant}$$

or

$$P_1V_1 = P_2V_2$$

Charles's Law

- Charles (1787) and Gay-Lussac (1822) kept the mass of gas and the pressure constant and studied the relationship between temperature and volume

They found $\dfrac{V_{(100^o C)}}{V_{(0^o C)}} = 1.375$

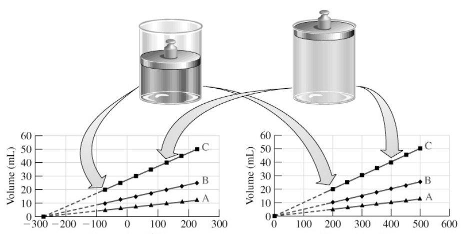
Charles's Law

- Further experiments showed that volume and temperature were linearly related and that the temperature intercept (when volume is zero) was at –273.15°C.
- This temperature is now defined as absolute zero and the Kelvin temperature scale given by

$T(K) = t(^oC) + 273.15$

Charles's Law

- Graphically:



Charles's Law/Combined Gas Law

Charles's Law can be expressed as $\frac{V}{T} = \text{constant}$

Combining Boyle's Law and Charles's Law

$P.V = \text{constant}$ and $\frac{V}{T} = \text{constant}$

gives

$$\frac{P.V}{T} = \text{constant} \quad \text{or} \quad \frac{P_1.V_1}{T_1} = \frac{P_2.V_2}{T_2}$$

Avogadro's Law

- From Gay-Lussac's experiment on reacting gases Avogadro concluded
  - "Equal volumes of different gases, at the same temperature and pressure, contain equal numbers of molecules"
- Extending this to a consideration of adding volumes of gases- one concludes that gas volume is proportional to number of molecules and subsequently to number of moles.

$$V \propto n \text{ or } V/n = \text{constant}$$

Gas Law

Given that :

$P.V = \text{constant}$ (Boyle's Law)

$\frac{V}{T} = \text{constant}$ (Charles's Law)

$\frac{V}{n} = \text{constant}$ (Avogadro's Law)

leads to

$\frac{P.V}{n.T} = \text{constant}$ Usually written **PV = nRT**

(Where R is a constant)

Ideal Gas Law

- The ideal gas law can be written in terms of moles or molecules

$PV = nRT$
n=number of moles R= Gas constant

$PV = NkT$
N=number of molecules k= Boltzmann's constant

Ideal Gas Law

- Values of the constants
  - $R = 8.314\ J\ K^{-1}\ mol^{-1}$ ($Pa\ m^3\ K^{-1}\ mol^{-1}$, *$kPa\ L\ K^{-1}\ mol^{-1}$*)
    $R = 0.0821\ L\ atm\ K^{-1}\ mol^{-1}$
  - $k = 1.38 \times 10^{-23}\ J\ K^{-1}$ (really $J\ K^{-1}\ molecule^{-1}$ but molecule is just a number)

Other useful forms of the ideal gas law

$$PV = \frac{m}{M}RT$$ m = mass of gas

M = molar mass (molecular weight)

$$d_{gas} = \frac{m}{V} = \frac{PM}{RT}$$

Dalton's Law

- In a gas mixture each component fills the container and exerts the pressure it would if the other gases were not present.
- Alternatively, each component acts as if it were alone in the container

Dalton's Law

- Thus for any component i

$$P_iV = n_iRT$$

We call P_i the partial pressure of component i

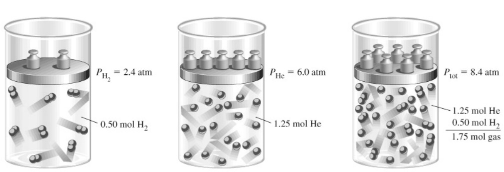
- The total pressure is given by the sum of the partial pressures

$$P = P_1 + P_2 + P_3 + \ldots.$$

- Also note that the mole fraction in the gas phase

$$\chi_i = \frac{n_i}{n} = \frac{P_i}{P}$$

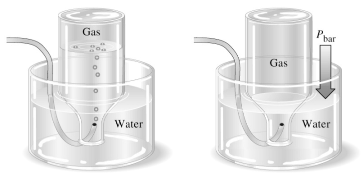
Dalton's Law



(a) 5.0 L at 20 °C (b) 5.0 L at 20 °C (c) 5.0 L at 20 °C

Dalton's Law

- A common use of Dalton's Law is when gases are collected over water



$P_{sample} + P_{water} = P_{bar}$