Ideal Gas Law

Relates pressure of a gas to temperature. For example, in a fixed volume, like a sealed bottle, pressure increases if temperature increases:

"P is proportional to T"

It is also known (called "Avogadro's Law") that pressure depends on the number of gas molecules present.

"P is proportional to N/V" (n = N/V = "number density")

Combining these, we have the "Ideal Gas Law"

$$P = (\text{constant}) \times (N/V) \times T$$
$$PV = NRT$$

Where "R" is the gas constant, 0.082 L atm mole^{-1} K^{-1}

$$P = (N/V)RT$$

There are many ways to write the ideal gas law. They are all equivalent. They just assume different units or dimensions.

For the atmosphere, where confined volumes are rare, we will use the density formulation. That is

$$P = [M]\,RT = \rho\,RT$$

[M] will be number density (in molecules cm^{-3})
ρ will be in g cm^{-3} or kg m^{-3}

To convert between these, we just need to express R in the proper units. In Problem 5, we derived an expression that gives us [M] from pressure (in mbar) and temperature (in Kelvin):

$$[M]\ (\text{in molec cm}^{-3}) = P/(RT) = 7.25 \times 10^{18}\ P(\text{mbar})/T(\text{K})$$

Units for chemical species

Concentration: [X], molecules cm^{-3}

(where we reserve "[M]" for the concentration of air – the sum of all compounds)

Mixing ratio (also called mixing fraction), [X] / [M]

Parts per million (ppm) = 1 in 10^6 (so multiply the mixing fraction by one million)

Parts per billion (ppb) = 1 in 10^9 (multiply by one billion)

Parts per trillion (ppt) = 1 in 10^{12} (multiply by one trillion).

For ppm, think of "parts of molecule X out of a million molecules of air"

We often write "ppmv" to express the fraction by number. This is because the volume of a gas and number density are related to each other by the ideal gas law.

To determine mixing ratio"by mass" (e.g., ppbm), we divide the mass of X by the total mass of air (m_X/m_{tot}). This isn't used as often (although it's popular for water vapor). This is because the rates of chemical reactions depend on number densities, and there aren't that many properties of air that depend on mass (although our next problem will!).

Pressure is expressed in a bewildering array!

Pressure = force per unit area

$P = F/A = (kg\ m\ s^{-2}) / (m^2) = kg\ m^{-1}\ s^{-2}$

The SI unit of pressure is the Pascal (Pa): $1\ Pa = 1\ N\ m^{-2}$

1 atm = 1 bar = 1000 mbar = 760 torr = 760 mm Hg
= 29.9 in Hg = 14.7 psi

More precisely,

$1\ atm = 1013.25\ mb = 1.01325 \times 10^5\ Pa$

Which units are used depends on field and country?

Meteorology: mbar (mb), hPa

Chemistry: torr or atm

TV weather: inches of Hg

The barometric law (hydrostatic balance, etc. etc.)

Why we care – in order to calculate the rates of chemical reactions, we will need the concentration of reactants, and usually, these are expressed in mixing ratio, which is dimensionless. We need to multiply by the number density of air, [M], in order to calculate the concentration of the molecules of interest. From Homework Problem 5, we note that in order to do this, we need temperature and pressure. Pressure decreases with altitude, so we need to find a quick way to estimate the pressure at any altitude. This will be the 'hydrostatic equation' which is used often in atmospheric sciences.

We can estimate the pressure at any altitude from a simple formula – one that isn't so simple to derive, but pretty easy to use.

$$P = P_o \, e^{(-z/H)}$$

How did we get the value for H?

$$H = RT/g$$

For an average temperature of about 250 K (we'll see where this number comes from next week)

$$H = (0.082\ \mathrm{L\ atm\ mol^{-1}\ K^{-1}}) \times (250\ \mathrm{K}) / (9.8\ \mathrm{m\ s^{-2}})$$

To simplify this, we note the following:

Air weighs 28.9 g $\mathrm{mol^{-1}}$ = 0.0289 kg $\mathrm{mol^{-1}}$

1 L = 1000 $\mathrm{cm^{-3}}$

1 atm = 1.01325×10^5 Pa = 101325 kg $\mathrm{m^{-1}\ s^{-2}}$

$$H = (0.082\ \mathrm{L\ atm\ mol^{-1}\ K^{-1}}) \times (1000\ \mathrm{cm^3\ L^{-1}}) \times (1/0.0289\ \mathrm{mol\ kg^{-1}}) \times (101325\ \mathrm{kg\ m^{-1}\ s^{-2}}) \times (10^{-6}\ \mathrm{m^3\ cm^{-3}}) \times (250\ \mathrm{K}) / (9.8\ \mathrm{m\ s^{-2}})$$

$$= 7.33 \times 10^3\ \mathrm{m} \sim 7\ \mathrm{km}$$

Problem: An airplane typically flies at 10 km (33,000 ft) altitude. What is the approximate pressure there?

$$P = P_o \exp(-z/H) = 1013 \text{ mb} \bullet \exp(-10/7) = 240 \text{ mb}$$

Note – this is about ¼ the pressure at sea level

On your own – repeat the calculation for the summit of Mt. Everest, which is at 29,000 feet. Why do you suppose most climbers use bottles of pure O_2?

See Problem 8

Calculating Concentration from a Mixing Ratio
(This is similar to Problem 7, only in reverse)

Problem: The mixing ratio of water vapor in the stratosphere is about 5 ppmv. If the ambient temperature is 210 K and the pressure is 100 mbar, what is the concentration of water?

The mixing ratio of water is defined as $[H_2O]/[M]$. The mixing ratio is 5 ppmv = $5 / (1x10^6) = 5x\ 10^{-6}$

We must calculate [M] first. ($[M] = P/RT$)

From Homework 1, $[M] = (7.26 \times 10^{18}) \times (100\ \text{mbar}) / (210\ \text{K})$

$= 3.46 \times 10^{18}$ molec cm^{-3}

So $[H_2O] = (5 \times 10^{-6}) \times [M] = (5 \times 10^{-6}) \times (3.49 \times 10^{18})$ molec cm^{-3}

$= 1.75 \times 10^{13}$ molec cm^{-3}