

MOLECULAR MASSES

The System of Study: Let us postulate a system of study consisting of a p -population of gaseous atmospheric molecules in random motion in [proximity space](#). The surface of interest is the intangible surface of an imaginary sphere surrounded by the p -population.

Definition of Mean Molecular Mass: The mean molecular mass of this p -population is defined as:

$$\bar{m}_p = \frac{1}{N} \sum_1^N m_p \quad \text{MSS01}$$

Here, \bar{m}_p is the mean molecular mass in kilograms, N is the number of atmospheric gas molecules in the system, and m_p is the individual molecular mass in kilograms.

Variability of Molecular Masses

The molecules that make up our atmosphere have many different molecular masses. Nitrogen, the most common atmospheric gas has three different molecular masses. Oxygen, the next most common, has six. Argon has three. Carbon dioxide has twelve. Water vapor has nine different molecular masses. And these masses are just for the un-ionized atmospheric molecules. When you add in all the different masses of the atmospheric ions, the number of different molecular masses grows even greater.

Moreover, the proportions of the various gases in the free atmosphere vary from time to time and from place to place. Yes, there are standard mixing ratios and standard molecular masses for dry air and for water vapor. However, your chances of getting a random sample of the free atmosphere with the exact mean molecular mass as the standard value are slim, at best. There are several reasons for this.

Variability as a Function of Scale: Let's take a system sample of the free atmosphere. The system sample size is one cubic centimeter. The mean molecular mass of the cubic millimeter in that sample's upper northeast corner (test sample A) is very likely to be the same to within five significant figures, or more as the mean molecular mass of the cubic millimeter in the lower southwest corner (test sample B).

If we expand that system sample size to one cubic meter, the mean molecular masses of those two test samples in opposite corners will still (usually, but not always) match to within three significant figures. There are plenty of places within the free atmosphere where that match will only be to one significant figure¹.

Change our system sample size to one cubic kilometer, and matches to only one significant figure will be the norm.

Variability as a Function of Meteorological Processes: The most common cause of variability in mean molecular mass is simple changes in humidity. Anything that changes the ratio of water vapor to dry air will change the mean molecular mass significantly. Let us take a vertical column through the base of a simple cumulus cloud. The mean molecular mass of the air near the surface of the ground will differ from the air just under the base of the cloud. This, in turn, will differ from that within the cloud and from that a few meters above the cloud.

Water vapor ratios are not the only culprit. Concentrations of carbon dioxide, ozone, carbon monoxide, methane, and the like vary significantly from place to place and time to time within the atmosphere. Even the concentration of oxygen will vary from a crowded auditorium to the open ocean to a polar desert to the depths of a forest at night. Differences of composition with elevation appear when you leave the troposphere, and even at times within the troposphere.

This principle still holds true on a smaller scale. The air next to a rain drop will probably have a different mixing ratio (water vapor to dry air) than air some distance away. Condensing air around a cloud droplet at the base of a cloud will have a different mean molecular mass than evaporating air around a cloud droplet at the cloud's margin. And so on and so forth.

As a matter of fact, we can say with some confidence that whenever weather is occurring there exist many disparities in mean molecular masses from place to place and from time to time within that weather system.

Variability as a Function of Ecological Processes: A moment's thought will convince you that the air you exhale has a different mean molecular mass than the air you inhaled a moment earlier. It has a higher concentration of water vapor and carbon dioxide and a lower concentration of oxygen. Similarly, the air moving toward the ocean surface will usually have a different mean molecular

¹ It must be admitted that matches of only one significant figure are made more probable by the fact that the most common mean value, 4.81×10^{-26} kilograms per molecule, is reduced to a single significant figure match when compared to a sample whose mean mass has dropped by a mere four-tenths of one percent.

mass than the air moving away from that surface. This is also due to differing concentrations of water vapor and carbon dioxide.

This principle generally holds true for other landscapes as well. Forests absorb carbon dioxide and oxygen and release carbon dioxide and oxygen and water vapor. The proportions vary with time of day and time of year and weather conditions. Water bodies are both sources and sinks of both water vapor and carbon dioxide and other gases. Areas of decaying vegetation produce methane—as do large herds of ruminants (and the occasional human). Cities are enormous sources of all kinds of strange gases—in addition to the obvious water vapor, carbon dioxide and carbon monoxide.

The consequence of these three sources of mean mass variability is to make us extremely leery of using an overly precise value for the mean molecular mass of any portion of the free atmosphere.

Mean Molecular Masses

In the discussion above, we suggested caution in using a “one size fits all” mean molecular mass for the free atmosphere. This does not mean that we should not acknowledge standards. They are useful points of departure.

By taking many samples of atmospheric air at different places, different seasons, and different elevations, atmospheric scholars have arrived at a mean molecular value for dry tropospheric air. It is:

$$\bar{m}_p = 4.80985 \times 10^{-26} \text{ kilograms}$$

Here, the **dot** below the mass symbol denotes that the symbol refers to the mass of dry air only. A *tilde* (~) below the mass symbol would denote that the symbol referred only to water vapor. The mass symbol without anything at all beneath it refers to humid air. All significant parcels of the free atmosphere are composed of humid air. The *p* subscript denotes that the molecules are members of the *p*-population.

All tables may be found at the end of the text section. Table MSS01 shows how this mean molecular mass for dry air was reached. For each component gas of the atmosphere, the component name, chemical symbol, mean molecular mass, and mean atmospheric abundance are shown. Sources for these values can be found in the References section at the end of this paper.

The mean molecular mass for the water molecule is that specified by the Vienna Standard Mean Ocean Water (VSMOW) protocol. Its value is:

$$\bar{m}_p = 2.99150512 \times 10^{-26} \text{ kilograms}$$

In case you are wondering, the VSMOW standard is not unique to Vienna and has nothing to do with ocean water. It applies solely to fresh water of laboratory isotopic composition and purity. Once again, the p subscript denotes that the molecules are members of the p -population.

For humid air within the p -population, the mean molecular mass becomes:

$$\bar{m}_p = \frac{1}{p} (\bar{m}_p \bar{p} + \bar{m}_p \bar{p}) \quad \text{MSS02}$$

Isotopic Variations in Molecular Masses: Except for Iodine, every common atmospheric gas is present in two or more isotopes. Each of these isotopes has its own mass and its own atmospheric abundance. Table MMS02 shows these isotopes.

Carbon-14: Not included in the MMS02 listing because it is unstable is carbon-14, also known as radioactive carbon. This isotope is found in all atmospheric carbon compounds in the parts per trillion concentrations. Its half-life is on the order of 5,730 years. It is produced in the upper atmosphere by the bombardment of ^{14}N by cosmic rays; and decays back into ^{14}N by beta decay. In the form of carbon-dioxide, it dissolves in water and thence is taken up by all living things. After being “fixed” in these life forms it starts to decay at a predictable rate. By measuring the rate of decay, scholars can determine how long it has been since the isotope was fixed. The technique is useful for dating samples up to about 60,000 years old.

Abundance of Water Vapor in the Free Atmosphere: Studies suggest that water vapor makes up roughly four-tenths of one percent by volume of the atmospheric gases. Close to the surface, its abundance varies from virtually nil to several percent.

At an atmospheric temperature of 25°C, an atmospheric pressure of 100,000 Pascals, and a vapor pressure of 1,583.8 Pascals (50% RH), water vapor makes up an obvious 1.5838% by volume of the atmosphere where most of us live. This seems to me to be a useful working average for the anthroposphere.

Mean Molecular Impulse Masses

For the i -subpopulation of molecules (molecules temporarily interacting with the surface of interest), the mean molecular masses will be somewhat different. As we see in [Molecular Speeds](#), this is because this interactive population will have a higher proportion of faster molecules in its

impulse speed distribution than are found in the proximity speed distribution of the p -population. Higher speeds are more likely to be associated with lower masses.

We can state with some confidence that for almost every sample of air from the free atmosphere, the mean molecular impulse mass is less than the mean molecular proximity mass. That is,

$$\bar{m}_i < \bar{m}_p$$

The next step is to evaluate \bar{m}_i for dry air. To do that, we need to know how frequently the molecules of each of the various dry air isotopes hit a square meter of surface in one second of time. The frequency with which a molecular isotope strikes a surface is termed the molecular flux rate for that isotope. Borrowing the *universal flux rate* from [Molecular Flows](#) gives us:

$$\bar{f}_{iso} = \bar{n}_{iso} \bar{v}_{iso} \quad \text{MSS03}$$

In this specific case, \bar{f}_{iso} is the isotopic flux in number of impacts per square meter of surface per second, \bar{n}_{iso} is the isotopic number density in number of isotopic molecules per cubic meter with a component of translatory movement normal to and toward the surface, and \bar{v}_{iso} is the mean translational isotopic proximity speed in meters per second normal to and toward the surface.

We may safely substitute isotopic abundance for \bar{n}_p if we keep our equations normalized. To evaluate \bar{v}_{iso} , we borrow from [Molecular Speeds](#) the equivalence:

$$\bar{v}_{iso} = \sqrt{\frac{2}{\pi}} \sigma \quad \text{MSS04}$$

Here, σ is [sigma](#), the standard deviation of the proximity speed distribution (dn/dv_p). We can evaluate σ by borrowing from [Kinetic Energies of Translation](#) the equivalence:

$$m_{iso} \sigma^2 = k_B \bar{T} \quad \text{MSS05}$$

In this specific case, m_{iso} is the singular isotopic mass in kilograms, k_B is Boltzmann's Constant in joules per molecule per Kelvin, and \bar{T} is the isotopic gas temperature in Kelvins.

For each isotope, we now have the mean isotopic speed:

$$\bar{v}_{iso} = \left(\frac{2k_B \bar{T}}{\pi m_{iso}} \right)^{\frac{1}{2}} \quad \text{MSS06}$$

The frequency with which each isotope impacts upon a surface thus becomes:

$$\bar{f}_{iso} = A\bar{v}_{iso} \quad \text{MSS07}$$

Here, A is the isotopic abundance shown in Table MSS02.

To get the mean value (\bar{v}_{iso}^{Σ}) for all ninety-five isotopes, we sum all ninety-five of the individual fluxes, and divide by the total abundance (unity). That is:

$$\bar{v}_{iso}^{\Sigma} = \sum_1^{95} \bar{f}_{iso} \quad \text{MSS08}$$

We then convert this new value of \bar{v}_{iso}^{Σ} into the equivalent value of σ .

$$\sigma = \sqrt{\frac{\pi}{2}} \bar{v}_{iso}^{\Sigma} \quad \text{MSS09}$$

We can now obtain the value of \bar{m}_{iso}^{Σ} .

$$\bar{m}_{iso}^{\Sigma} = \frac{k_B \bar{T}}{\sigma^2} \quad \text{MSS10}$$

After all of this, it turns out that the value of the mean impulse mass for the mixture of ninety-five dry air isotopes is:

$$\bar{m}_i = 47.9514505 \times 10^{-27} \text{ kilograms}$$

This compares to the mean molecular proximity mass for dry air of:

$$\bar{m}_p = 48.0985096 \times 10^{-27} \text{ kilograms}$$

This is only a diminution of barely under one percent over the mean dry air molecular mass. Still, it is a diminution.

It should be noted that—despite the use of the temperature term in the above equations—the mean impulse mass is independent of temperature. It is purely a function of the individual isotopic masses and the individual isotopic abundances.

Mean Impulse Mass of Water Vapor: Following the identical procedure for water vapor, we arrive at the mean molecular impulse mass of:

$$\bar{m}_i = 29.9144976 \times 10^{-27} \text{ kilograms}$$

This compares to the mean molecular mass of:

$$\bar{m}_p = 29.9150512 \times 10^{-27} \text{ kilograms}$$

The very slight diminution (less than nineteen parts per million) is a consequence of the fact that the most common isotope of water makes up a full 99.73% of all water vapor molecules.

Significance of the Mean Impulse Mass: It should be noted that the mean impulse mass should always be used in preference to the mean molecular mass whenever we calculate parameters involving molecular passages or other interactions with a surface of interest; such as impacts, collisions, diffusion, kinetic energies, and the like. The mean molecular proximity mass (\bar{m}_p) is useful only for calculating [atmospheric mass density](#). Both the pressure parameter and the temperature parameter make use of the mean impulse mass; and make no use of the mean molecular mass.

Of course, if you only use three significant figures in your calculations, the argument becomes moot—most of the time!

Molecular Masses in Moving Air: Molecular mass is not affected by either wind speed or wind direction.

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TABLES

TABLE MSS01 - MEAN MOLECULAR MASSES OF DRY AIR

COMPONENT GAS	ATMOSPHERIC ABUNDANCE	MASS NUMBER (u)	MEAN MOLECULAR MASS x 10 ⁻²⁷ kg
Nitrogen	0.780795000000	28.013400	46.517
Oxygen	0.209447777200	31.998800	53.135
Argon	0.009340000000	39.947800	66.335
Carbon Dioxide	0.000390000000	44.009500	73.079
Neon	0.000018180000	20.179700	33.509
Helium	0.000005240000	4.002602	6.646
Methane	0.000001790000	16.042460	26.639
Krypton	0.000001140000	83.798000	139.150
Hydrogen	0.000000550000	2.158800	3.585
Nitrous Oxide	0.000000300000	44.012800	73.085
Carbon Monoxide	0.000000010000	28.010100	46.512
Xenon	0.000000009000	131.293000	218.017
Ozone	0.000000003500	47.998200	79.703
Nitrogen Dioxide	0.000000000200	46.005500	76.394
Iodine	0.000000000100	253.808940	421.460
Dry Air	1.000000000000	28.965604	48.0985

TABLE MSS02 - ISOTOPIC MASSES AND ABUNDANCES OF DRY AIR

COMPONENT GAS	SYMBOL	ISOTOPE	ISOTOPIC MASS x 10 ⁻²⁷ kg	ATMOSPHERIC ABUNDANCE
Nitrogen	N ₂	¹⁴ N ¹⁴ N	46.50529	0.775121158
		¹⁴ N ¹⁵ N	48.16091	0.005663497
		¹⁵ N ¹⁵ N	49.81653	0.000010345
Oxygen	O ₂	¹⁶ O ¹⁷ O	54.78789	0.000158794
		¹⁶ O ¹⁸ O	56.44848	0.000856649
		¹⁷ O ¹⁷ O	56.45543	0.000000030
		¹⁷ O ¹⁸ O	58.11602	0.000000326
		¹⁸ O ¹⁸ O	59.77661	0.000000880
Argon	Ar	³⁶ Ar	59.72550	0.000031158
		³⁷ Ar	63.03859	0.000005875
		³⁸ Ar	66.35909	0.009302967
Carbon Dioxide	CO ₂	¹² C ¹⁶ O ¹⁶ O	73.04682	0.000383954
		¹² C ¹⁶ O ¹⁷ O	74.71436	0.000000293
		¹² C ¹⁶ O ¹⁸ O	76.37495	0.000001578
		¹² C ¹⁷ O ¹⁷ O	76.38190	<1 ppb
		¹² C ¹⁷ O ¹⁸ O	78.04249	0.000000001
		¹² C ¹⁸ O ¹⁸ O	79.70308	0.000000002
		¹³ C ¹⁶ O ¹⁶ O	74.71293	0.000004153
		¹³ C ¹⁶ O ¹⁷ O	76.38047	0.000000003
		¹³ C ¹⁶ O ¹⁸ O	78.04106	0.000000017
		¹³ C ¹⁷ O ¹⁷ O	78.04801	<1 ppb
	¹³ C ¹⁷ O ¹⁸ O	79.70860	<1 ppb	
	¹³ C ¹⁸ O ¹⁸ O	81.36918	<1 ppb	
Neon	Ne	²⁰ Ne	33.19822	0.000016449
		²¹ Ne	34.86110	0.000000049
		²² Ne	36.51755	0.000001682
Helium	He	³ He	5.008234	<1 ppb
		⁴ He	6.646478	0.000005240
Methane	CH ₄	¹² CHHHH	26.62060	0.000001770
		¹² CHHHD	28.29156	0.000000001
		¹² CHHDD	29.96252	<1 ppb

COMPONENT GAS	SYMBOL	ISOTOPE	ISOTOPIC MASS x 10 ⁻²⁷ kg	ATMOSPHERIC ABUNDANCE
Methane (cont.)		¹² CHDDD	31.63348	<1 ppb
		¹² CDDDD	33.30444	<1 ppb
		¹³ CHHHH	28.28671	0.000000019
		¹³ CHHHD	29.95767	<1 ppb
		¹³ CHHDD	31.62863	<1 ppb
		¹³ CHDDD	33.29959	<1 ppb
		¹³ CDDDD	34.97055	<1 ppb
Krypton	Kr	⁷⁸ Kr	129.898	0.000000004
		⁸⁰ Kr	132.042	0.000000026
		⁸² Kr	136.205	0.000000132
		⁸³ Kr	137.821	0.000000131
		⁸⁴ Kr	139.383	0.000000650
		⁸⁶ Kr	142.579	0.000000197
Hydrogen	H ₂	HH	3.347065	0.000000550
		HD	5.018027	<1 ppb
		DD	6.688988	<1 ppb
Nitrous Oxide	N ₂ O	¹⁴ N ¹⁴ N ¹⁶ O	73.06547	0.000000297
		¹⁴ N ¹⁴ N ¹⁷ O	74.73301	<1 ppb
		¹⁴ N ¹⁴ N ¹⁸ O	76.39360	0.000000001
		¹⁴ N ¹⁵ N ¹⁶ O	74.72109	0.000000002
		¹⁴ N ¹⁵ N ¹⁷ O	76.38863	<1 ppb
		¹⁴ N ¹⁵ N ¹⁸ O	78.04921	<1 ppb
		¹⁵ N ¹⁴ N ¹⁶ O	76.37670	<1 ppb
		¹⁴ N ¹⁵ N ¹⁷ O	78.04424	<1 ppb
		¹⁵ N ¹⁵ N ¹⁸ O	79.70483	<1 ppb
Carbon Monoxide	CO	¹² C ¹⁶ O	46.48664	0.000000010
		¹² C ¹⁷ O	48.15418	<1 ppb
		¹² C ¹⁸ O	49.81477	<1 ppb
		¹³ C ¹⁶ O	48.15275	<1 ppb
		¹³ C ¹⁷ O	49.82029	<1 ppb
		¹³ C ¹⁸ O	51.48088	<1 ppb
Xenon	Xe	¹²⁴ Xe	205.7505	<1 ppb
		¹²⁶ Xe	209.0689	<1 ppb

COMPONENT GAS	SYMBOL	ISOTOPE	ISOTOPIC MASS x 10 ⁻²⁷ kg	ATMOSPHERIC ABUNDANCE
Xenon (continued)		¹²⁸ Xe	212.3888	<1 ppb
		¹²⁹ Xe	214.0514	0.000000002
		¹³⁰ Xe	215.7098	<1 ppb
		¹³¹ Xe	217.3730	0.000000002
		¹³² Xe	219.0320	0.000000002
		¹³⁴ Xe	222.3551	0.000000001
		¹³⁶ Xe	225.6792	0.000000001
Ozone	O ₃	¹⁶ O ¹⁶ O ¹⁶ O	79.68053	0.000000003
		¹⁶ O ¹⁶ O ¹⁷ O	81.34807	<1 ppb
		¹⁶ O ¹⁶ O ¹⁸ O	83.00866	<1 ppb
		¹⁶ O ¹⁷ O ¹⁷ O	83.01561	<1 ppb
		¹⁶ O ¹⁷ O ¹⁸ O	84.67620	<1 ppb
		¹⁶ O ¹⁸ O ¹⁸ O	86.33679	<1 ppb
		¹⁷ O ¹⁷ O ¹⁷ O	84.68315	<1 ppb
		¹⁷ O ¹⁶ O ¹⁸ O	86.34374	<1 ppb
		¹⁷ O ¹⁸ O ¹⁸ O	88.00433	<1 ppb
		¹⁸ O ¹⁸ O ¹⁸ O	89.66491	<1 ppb
Nitrogen Dioxide	NO ₂	¹⁴ N ¹⁶ O ¹⁶ O	76.37300	<1 ppb
		¹⁴ N ¹⁶ O ¹⁷ O	78.04054	<1 ppb
		¹⁴ N ¹⁶ O ¹⁸ O	79.70113	<1 ppb
		¹⁴ N ¹⁷ O ¹⁷ O	79.70808	<1 ppb
		¹⁴ N ¹⁷ O ¹⁸ O	81.36867	<1 ppb
		¹⁴ N ¹⁸ O ¹⁸ O	83.02926	<1 ppb
		¹⁴ N ¹⁶ O ¹⁶ O	78.02861	<1 ppb
		¹⁴ N ¹⁶ O ¹⁷ O	79.69616	<1 ppb
		¹⁴ N ¹⁶ O ¹⁸ O	81.35674	<1 ppb
		¹⁴ N ¹⁷ O ¹⁷ O	81.36370	<1 ppb
		¹⁴ N ¹⁷ O ¹⁸ O	83.02428	<1 ppb
		¹⁴ N ¹⁸ O ¹⁸ O	84.68487	<1 ppb
Iodine	I ₂	¹²⁷ I ¹²⁷ I	421.45960	<1 ppb

**TABLE MSS03 - ISOTOPIC MASSES AND ABUNDANCES OF WATER VAPOR
(VSMOW)**

GAS	SYMBOL	ISOTOPE	ISOTOPIC MASS x 10 ⁻²⁷ kg	ISOTOPIC ABUNDANCE
Water Vapor	H ₂ O	HH ¹⁶ O	29.9072411	0.997309885333
		HD ¹⁶ O	31.5782027	0.000310690470
		DD ¹⁶ O	33.2491643	0.000000024197
		HH ¹⁷ O	31.5747826	0.000378881958
		HD ¹⁷ O	33.2457441	0.000000118033
		DD ¹⁷ O	34.9167057	0.000000000009
		HH ¹⁸ O	33.2353700	0.001999776964
		HD ¹⁸ O	34.9063315	0.000000622988
		DD ¹⁸ O	36.5772931	0.000000000049
VSMOW	H ₂ O	-	29.9150512	1.000000000000

REFERENCES

Internal References: References to other essays in this collection are linked in the essay text by hyperlinks. You may follow these hyperlinks or ignore them, as you choose.

External References: These are papers by other authors that contain statements or data that are specifically incorporated into this essay.

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General References: These are works that I have read carefully and whose views have helped to shape the views presented in this collection. None of these authors are have any responsibility for my many unconventional views and opinions.

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Table MMS01 Methodology: The starting point was the table in the Wikipedia article. Abundances in this table totaled greater than unity. Consequently, abundances for nitrogen and oxygen were reduced proportionately so that the total abundance equaled unity.

Computational System: All calculations were carried out by Microsoft's© Excel Program 2003 (SP3).