MOLECULAR NUMBERS

Definition of Number Density – Let us start our discussion of molecular numbers with the most basic molecular number—mean number density. Let us postulate that some portion of our system of atmospheric gas molecules contains N gas molecules and occupies V cubic meters of volume. The mean number density is very simply derived, and is

$$\bar{n} = \frac{N}{V} \qquad\qquad \text{MNS01}$$

Here, the mean number density $\bar{n}$ has the dimensions of NL^{-3}, and is presented in terms of number of gas molecules per cubic meter.

This is a mean number because, for atmospheric air, its magnitude is on the order of 10^{25} molecules per cubic meter. Statistical mechanics tells us that odds that any exact number (to all twenty-six significant figures) should persist in any given cubic meter of air from one time segment to another is vanishingly small.

Number Density in Ideal Gases – If our air were still, we could also derive the mean number density from the thermodynamic version of the Ideal Gas Equation of State (see **Gas Laws in the Free Atmosphere**). That would give us:

$$\bar{n} = \frac{\bar{p}}{k_B \bar{T}} \qquad\qquad \text{MNS02}$$

Here, $\bar{p}$ is the mean air pressure in Pascals, $\bar{T}$ is the temperature in Kelvins, and $\mathbf{k_B}$ is Boltzmann's Constant in joules per molecule per degree.

This equation does not always work for real gases, especially at high densities. However, it works pretty well for air at the temperatures and pressures normally found in our atmosphere. Tables MNS01 and MNS02 are based on that

equation. All calculations for these two tables are based on the 2006 CODATA value for Boltzmann's Constant of 1.3806504 x 10^{-23} Joules per Kelvin per molecule.

TABLE MNS01

NUMBER DENSITY AT SELECTED VALUES
OF TEMPERATURE AND PRESSURE

SYSTEM TEMP	SYSTEM TEMP	THERMAL TERM	NUMBER DENSITY AT 1.01325 x 10^5 PASCALS	NUMBER DENSITY AT 1.00000 x 10^5 PASCALS
°C	$\overline{T}$	$k_B\overline{T}$	$\overline{n}$	$\overline{n}$
		x 10^{-21}	x 10^{25}	x 10^{25}
	K	J molecule^{-1}	molecules m^{-3}	molecules m^{-3}
75	348.15	4.8067	2.1080	2.0804
70	343.15	4.7377	2.1387	2.1107
65	338.15	4.6687	2.1703	2.1419
60	333.15	4.5996	2.2029	2.1741
55	328.15	4.5306	2.2365	2.2072
50	323.15	4.4616	2.2711	2.2414
45	318.15	4.3925	2.3068	2.2766
40	313.15	4.3235	2.3436	2.3129
35	308.15	4.2545	2.3816	2.3505
30	303.15	4.1854	2.4209	2.3892
25	298.15	4.1164	2.4615	2.4293
20	293.15	4.0474	2.5035	2.4707
15	288.15	3.9783	2.5469	2.5136
10	283.15	3.9093	2.5919	2.5580
5	278.15	3.8403	2.6385	2.6040
0	273.15	3.7712	2.6868	2.6516

TABLE MNS02

NUMBER DENSITY AT SELECTED VALUES
OF TEMPERATURE AND PRESSURE

SYSTEM TEMP	SYSTEM TEMP	THERMAL TERM	NUMBER DENSITY AT 1.01325 x 10^5 PASCALS	NUMBER DENSITY AT 1.00000 x 10^5 PASCALS
°C	$\bar{T}$	$k_B\bar{T}$	$\bar{n}$	$\bar{n}$
		x 10^{-21}	x 10^{25}	x 10^{25}
	K	J molecule^{-1}	molecules m^{-3}	molecules m^{-3}
0	273.15	3.7712	2.6868	2.6516
-5	268.15	3.7022	2.7369	2.7011
-10	263.15	3.6332	2.7889	2.7524
-15	258.15	3.5641	2.8429	2.8057
-20	253.15	3.4951	2.8990	2.8611
-25	248.15	3.4261	2.9575	2.9188
-30	243.15	3.3571	3.0183	2.9788
-35	238.15	3.2880	3.0816	3.0413
-40	233.15	3.2190	3.1477	3.1066
-45	228.15	3.1500	3.2167	3.1746
-50	223.15	3.0809	3.2888	3.2458
-55	218.15	3.0119	3.3642	3.3202
-60	213.15	2.9429	3.4431	3.3981
-65	208.15	2.8738	3.5258	3.4797
-70	203.15	2.8048	3.6126	3.5653
-75	198.15	2.7358	3.7037	3.6553

The numbers in these two tables are valid for any parcel of atmospheric air at the combinations of temperature and pressure shown above. They are valid all humidities and other variations in gaseous composition. They are valid for any isotopic variations.

The reason for this validity is one of the most important concepts in kinetic gas theory: Avogadro's Law.

Avogadro's Law

In effect, this law states that:

At any specific combination of temperature and pressure, the number of molecules per unit volume of any gas or any combination of non-reacting gases is the same.

This means that at any specific combination of temperature and pressure the number of molecules in one cubic meter is the same for dry air, for humid air, for air contaminated with industrial gases, for the air you inhale and for the air you exhale, for any air at all.

The only caveat is that the air must be still. It may not be moving. If there are any winds or currents or any other significant net air movement, the pressure is thrown out of whack, and all bets are off. We will deal with how pressure is affected by moving air in future essays.

The General Population (*p* subscript) – In ***The Two Populations***, we divided all of the gaseous air molecules of our system into two populations, the general population and the interactive population. The general population was further divided into two sub-populations based on direction of movement relative to an object of interest.

In both ideal gases and real gases, under conditions of equilibrium and under conditions of non-equilibrium, in still air and in moving air, when the object of interest is moving and when it is not, the two sub-populations of the general population must total that general population. That is,

$$\bar{n}_p + \bar{n}_{-p} = \bar{n} \qquad \text{MNS03}$$

Under conditions of equilibrium—and only under conditions of equilibrium—we can say that the number densities for our two p sub-populations are the same. That is,

$$\bar{n}_p = \bar{n}_{-p} = \tfrac{1}{2}\bar{n} \text{ (at equilibrium)} \qquad \text{MNS04}$$

For all intents and purposes, conditions of equilibrium can be considered to exist only in computer simulations and in the imagination of scientists. In the free atmosphere, both natural phenomena and the mathematics of probability make sure that it never happens. When your instruments say that equilibrium exists, this will always be a case of instrumental insensitivity, not true equilibrium. What we have then is quasi-equilibrium, not true equilibrium.

These two sub-populations will not even be in quasi-balance under normal atmospheric conditions. Whenever heating or cooling is taking place, the two sub-populations will be unequal. Whenever either evaporation or condensation is taking place, the two sub-populations will be unequal. Wherever we have sources or sinks of atmospheric gases, the two sub-populations will be unequal. Whenever the atmosphere is in even the slightest fluid movement, the two sub-populations will be unequal. In short, forget about finding the two sub-populations equal.

The safest assumption is,

$$\bar{n}_p \neq \bar{n}_{-p} \qquad \text{MNS05}$$

The Interacting Population (i subscript) – In the interactive population, molecular numbers do not refer to populations at some given instant, but to flow rates toward or through some unit of area in some measure of time. As such, they are not primary parameters, but secondary ones. These molecular flows are dealt with in *Molecular Flows*.

Molecular Numbers in Moving Air – When the wind is blowing, both the numbers of molecules moving in any particular direction and the speeds and velocities with which they move will change. These changes will be functions of both the wind velocity and the direction in which the wind is blowing relative to the object of interest.

In addition, turbulence brings about rapid and significant changes in mass density of moving air. This, of course, affects the number density as well. Although most of these density changes are ephemeral, some last for significant periods of time.

The relationships are extremely complex, and will be discussed in future papers.

Back to **Basic Parameters Menu**

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REFERENCES

INTERNAL REFERENCES: These are other papers in this collection that are either cited or linked during the course of the discussion or whose content is especially relevant to the current discussion.

Gas Laws in The Free Atmosphere: This paper shows how many of the gas laws useful and valid in the laboratory are neither when applied to the free atmosphere. Many gas laws require that the parcel of air be in a state of equilibrium. The atmosphere is never really in a state of equilibrium—certainly not when weather is occurring. Some gas laws require keeping one parameter constant while varying another. This is not possible in the free atmosphere.

The Two Populations – This paper introduces the general population and the interacting population.

Molecular Flows – This paper defines the flow parameter ($\overline{f}_i$) and shows how it is derived. The concept of a Universal Flux Equation is introduced.

The Probability Density Curve – This paper discusses the significance and history of the probability density curve. It goes on to show how in its normalized form it is also the distribution function for axial velocities.

The Nature of Atmospheric Pressures – This paper defines gas pressures ($\overline{p}$) in terms of kinetic gas theory and statistical mechanics. The Universal Pressure Equation is introduced.

The Nature of Atmospheric Temperatures – This paper develops a universal gas temperature ($\overline{T}$) equation and shows how the ideal gas definition is a special case of the universal equation.

EXTERNAL REFERENCES: These are papers by other authors that contain statements or data that are specifically incorporated into the current discussion.

Fundamental Physical Constants: 2006 CODATA – Peter J. Mohr, Barry N. Taylor, and David B. Newell; National Institute of Science and Technology (NIST), *CODATA Recommended Values of the Fundamental Physical Constants: 2006;* Gaithersburg, 2007.
http://physics.nist.gov/cuu/Constants/codata.pdf

GENERAL REFERENCES: These are works by other authors that contain general treatments of kinetic gas theory, statistical mechanics and thermodynamics, atmospheric physics, and other scientific fields that are used in the current discussion.

Computational System: All calculations were carried out by Microsoft's© Excel Program 2003 (SP3). The reader should be alerted to the fact that this computational system uses fifteen significant figures for all calculations—whether or not such precision is warranted by the accuracy of the data.

Arthur Brown; **Statistical Physics**; Elsevier, New York, 1970.

D. Tabor; **Gases, Liquids, and Solids**; Third Edition; Cambridge University Press, 1991.

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