EQUILIBRIUM AND QUASI-EQUILIBRIUM

Many of the equations used in atmospheric physics require that conditions of equilibrium must exist within the system for the equations to be valid. These equations include most of the equations used to describe and define the gas laws. If equilibrium does not exist, then these gas laws are not reliable descriptors of system reality.

Definition of Condition of Equilibrium: For the essays in this collection, we shall postulate that equations requiring conditions of equilibrium to be valid need only balance to the conventional proper order of magnitude and three significant figures. If that conventional level of scientific accuracy and precision is met, then a condition of equilibrium exists.

Definition of Condition of Non-Equilibrium: If the any of the variables in any of these equations is changing in a manner that imbalances the equation, equilibrium does not exist. If there are winds or air currents—no matter how slight—equilibrium does not exist. If there are changes of phase at any level, equilibrium does not exist. If there is virtually any kind of weather phenomena at all, equilibrium does not exist.

Unfortunately, virtually all weather phenomena—the focus of most scholars in the various fields of the atmospheric sciences—are non-equilibrium phenomena. But then, nobody said that the study of the atmosphere was easy.

Definition of Quasi-Equilibrium: One way to get around the problem of a non-equilibrium atmosphere is to define a condition of "quasi" equilibrium where the equations will work well enough for our (not too picky) purposes and is common enough in the free atmosphere to be useful. Quasi-equilibrium may be said to exist whenever the following three conditions are met:

1. The equation $\bar{p} = \bar{n}\mathbf{k_B}\bar{T}$ is mathematically valid to three significant figures. Here, $\bar{p}$ is the ambient air pressure in pascals, $\bar{n}$ is the mean molecular number density in number of molecules per cubic meter, $\mathbf{k_B}$ is Boltzmann's Constant in joules per molecule per Kelvin, and $\bar{T}$ is the mean ambient air temperature in Kelvins.

2. There is no perceptible flow of air. This means no winds or air currents within the ambient system that would cause a leaf to quiver, a blade of grass to move, or a strand of gossamer to move in any direction but straight down.

3. Small ongoing changes in ambient temperature or ambient pressure or both are balanced by corresponding changes in the ambient number density.

The validity of $\bar{p} = \bar{n}\mathrm{k_B}\bar{T}$ under conditions of quasi-equilibrium is helped enormously by the extremely rapid response of ***n*** to changes in air temperature and pressure. In room-size volumes of air, this response is of the order of fractions of a second to reestablish equilibrium following normal and natural changes in air temperature and/or pressure.

This rapid response is due to three facts: 1) that mean molecular speeds are on the order of the speed of sound, and 2) the mean molecular flow rates are on the order of 3×10^{27} molecules per square meter per second, and 3) natural rates of change of air temperature and pressure are usually quite slight.

Uniformity under Conditions of Equilibrium: We must not make the mistake of assuming that under conditions of equilibrium that our system gas is also of uniform density. This is true, of course, on a gross macroscopic level. But, in a more fundamental sense, it is contrary to the essential premise of kinetic gas theory; that is, that a gas is composed of discrete particles surrounded by empty space.

Suppose that we divide any unit volume into $\bar{n}$ equal cells. We could then say that there would be an average of one molecule per cell. Although mathematically true, this statement is physically meaningless. Many cells would be empty at any given instant, while others would contain two or more molecules.

If there were exactly one molecule at the center of each cell, of course, then we could say that the molecules were evenly distributed. However, they are not evenly distributed—they are randomly distributed over both space and time. This distinction is an important one. It means that the number of molecules per cell will vary from cell to cell at a given instant of time, and from time to time within a given cell.

However, the probability of a cell containing a given number of molecules at a given instant in time remains constant and is the same for any cell of equal dimensions within the container. Likewise, the probability of a given cell containing a given number of molecules during a given period is also the same for any equal period of time.

These two concepts—that of randomness and that of probability—form the foundations of kinetic gas theory. Under conditions of equilibrium, randomness is maximized and equations and measurements based on probability theory adopt their most precise values.

Some Thoughts on Equilibrium: The reader should bear in mind that conditions of true equilibrium may be closely approximated in the laboratory, but are virtually impossible to find in any significant mass of air in the free atmosphere.

WARNING! Literature on the atmospheric sciences frequently contains statements to the effect that the gases of the atmosphere behave essentially as ideal gases under the conditions of temperature and pressure normally encountered in the troposphere. This is usually done when the author wants to use ideal gas equations to explain some aspect atmospheric behavior. (I do it myself!)

It is interesting to note that I have never encountered this statement when it was accompanied by the usual and customary scientific citations, attributions, and references.

What is often meant by that assertion is that small gradual changes in the parameters of equation $\bar{p} = \bar{n}\mathbf{k}_B\bar{T}$ can take place within parcels of atmospheric air without affecting its validity. As mentioned above, this is due to the extremely rapid response time of the $\bar{n}$ parameter to changes in $\bar{p}$ and $\bar{T}$.

It is also true that when a sample of atmospheric air is cleansed of all non-gaseous components (there go all clouds, rain, snow, fog, mist, colorful sunsets and rainbows), dehumidified (there goes most of the rest of our weather—as well as 60% of the atmosphere's heat budget), and de-ionized (there goes lightning, the Aurora Borealis, and the ionosphere), the resulting mixture of gases in the laboratory container (no winds there) do behave somewhat as ideal gases under a strictly limited range of temperatures and pressures.

However, any similarity between this laboratory sample and the free atmosphere is a great deal less than that between a neutered lap-dog and a pack of wild wolves. The gases of the free atmosphere (especially water vapor) do not behave as ideal gases. This statement will be supported by abundant evidence and illustrations in more advanced essays.

In short, dry air may occasionally behave as an ideal gas under strictly controlled laboratory conditions. Humid air will do so less often. Dirty, humid, ionized atmospheric air in the free and unconstrained atmosphere rarely behaves as an ideal gas in any significant way.

In fact, most weather consists of the atmosphere ***not*** behaving as an ideal gas—and most definitely **not** being under conditions of equilibrium. Equilibrium and weather are mutually exclusive conditions.

Summary: The global atmosphere is always in a state of non-equilibrium. It is never in either a state of true equilibrium or in a state of quasi-equilibrium. That is because extremely violent non-equilibrium weather phenomena are always occurring in one place within that global atmosphere or another—usually in several places at any given instant.

Relatively small parcels of free atmospheric air may be found under conditions of quasi-equilibrium. The spatial dimensions of these quasi-equilibrium parcels are normally measured in meters (not kilometers) and their temporal dimensions are normally measured in minutes (not hours).

Even smaller parcels of atmospheric air may be constrained under laboratory conditions. There, again, conditions of true equilibrium will never exist. However, very precise conditions of

quasi-equilibrium may be obtained for extended periods of time. Quite often, results that are accurate to six or more significant figures may be obtained. Care must be taken in applying the results of experiments on constrained air (especially dry air) to the uncontrolled and humid free atmosphere.

Thought experiments, where the values of all the system parameters are postulated, are useful ways of examining hypotheses. Here, the precision of values is unlimited since they do not apply to the real world.

