EQUILIBRIUM AND QUASI-EQUILIBRIUM

Many of the equations used in atmospheric physics require that conditions of equilibrium must exist within that atmosphere (or any significant portion of it) in order 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 atmospheric reality.

Unfortunately, virtually all weather phenomena—the focus of most scholars in the various fields of the atmospheric sciences—are non-equilibrium phenomena. Also, unfortunately, the laws of probability as exemplified in statistical mechanics tell us that true equilibrium in a molecular universe (or anything close to true equilibrium) is so unlikely as to be virtually impossible.

This is probably a good as place as any to define our terms. I should like to propose three different grades of equilibrium, ranging from the impossible to the occasional.

MOLECULAR EQUILIBRIUM – Under molecular equilibrium, the following three equations are valid to the proper order of magnitude and to as many significant figures as that order requires.

$$\bar{\boldsymbol{f}}_{+i} = \bar{\boldsymbol{f}}_{-i} \qquad \text{EAQ01}$$

$$\bar{\boldsymbol{\varphi}}_{+i} = \bar{\boldsymbol{\varphi}}_{-i} \qquad \text{EAQ02}$$

$$\bar{\boldsymbol{u}}_{+i} = \bar{\boldsymbol{u}}_{-i} \qquad \text{EAQ03}$$

Here $\bar{\boldsymbol{f}}$ is the mean molecular flow rate in number of molecules per square meter per second (28 significant figures), $\bar{\boldsymbol{\varphi}}$ is the mean molecular impulse in newtons

(23 significant figures), and $\bar{u}$ is the mean kinetic energy of translation in joules (21 significant figures).

The laws of probability tell us that the chances of this occurring in any portion of the free atmosphere at any time are so slight that the only English word that could accurately describe it is ***never***. For all intents and purposes molecular equilibrium does not occur in the known universe.

OPERATIONAL EQUILIBRIUM – For operational equilibrium to exist, three conditions must be met:

1. The following equation must be valid to three (3) significant figures and the proper orders of magnitude throughout the period of observation:

$$\bar{p} = \bar{n} \mathrm{k_B} \bar{T} \qquad \text{EAQ04}$$

Here $\bar{p}$ is the mean atmospheric pressure in Pascals, $\bar{n}$ is the mean molecular number density in number of molecules per cubic meter of air, $\mathrm{k_B}$ is Boltzmann's Constant in joules per molecule per degree, and $\bar{T}$ is the mean atmospheric temperature in Kelvins.

2. The mathematical value (to three significant figures) of each of the three variables in Equation EAQ04 must remain constant throughout the period of observation.

3. There must be no perceptible flow of air.

Generally speaking, operational equilibrium is far more readily attained in the laboratory than it is in the free atmosphere.

QUASI-EQUILIBRIUM – Conditions of quasi-equilibrium in the free atmosphere are far more common than conditions of operational equilibrium. However, they can only be found when no "weather" (as the various meteorological services define the term) is occurring. This is still not very often. Generally speaking, some sort of weather is almost always occurring.

For quasi-equilibrium to exist, we also have three necessary conditions:

1. Equation EAQ04 must be valid to three significant figures.

2. There must be no perceptible flow of air.

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

The validity of EAQ04 under conditions of quasi-equilibrium is helped enormously by the extremely rapid response of $\bar{n}$ 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 through a plane are on the order of 10^{27} molecules per square meter per second, whereas the actual number density is only on the order of 10^{25} molecules per cubic meter; and 3) natural rates of change of air temperature and pressure in the free atmosphere are usually quite slight—as long as no weather is occurring.

Summary: The global atmosphere is always in a state of non-equilibrium. It is never in either a state of operational 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 thousands of places at any given instant.

Relatively small parcels of free atmospheric air may be found under conditions of quasi-equilibrium and (less likely) operational equilibrium. The spatial dimensions of these parcels are normally measured in meters (not kilometers) and their temporal dimensions are normally measured in minutes (not hours). The standard scientific precision of three significant figures and the proper order of magnitude for the results of observations and measurements under conditions of quasi-equilibrium are usually the best that we can reasonably expect.

Even smaller parcels of atmospheric air may be constrained under laboratory conditions. There, again, conditions of molecular equilibrium will never exist. However, very precise conditions of operational 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 freely-flowing and humid real atmosphere.

Thought experiments, where the values of all of the state parameters and constants are postulated, are useful ways of examining hypotheses. Here, the precision of values is unlimited since they do not apply to the real world. For this same reason, these results should never be applied to the real world without testing in the free atmosphere.