

GAS LAWS IN THE FREE ATMOSPHERE

Meteorology, like Astronomy, is primarily an observational science rather than a laboratory science. This is because the complex mixture of gases, liquids, solids, charged particles, and photons that make up the free atmosphere behaves differently in the free state than when some small portion of it is abstracted, “cleaned up”, and subjected to laboratory constraints.

Moreover, many of the gas laws that apply to gases in laboratory containers are not applicable to the gases of the free atmosphere. There are three major reasons why many of these gas laws are generally inapplicable and a host of minor ones.

1. Specific Volume: Firstly, laboratory experiments are carried out in containers of various sizes and shapes; but all these containers have one thing in common. They have a specific volume. This volume is usually symbolized by V in the resulting equations. As a general rule, no gas law requiring a specific volume or equation containing a term denoting a specific volume may be applied to the free atmosphere.

Those of us who study the free atmosphere often refer to “masses” or “parcels” of air. We realize, however, that these entities have no fixed volume or even fixed boundaries. The molecules that make up a mass of air are continually diffusing out of the air mass; while molecules from the surrounding atmosphere are continually diffusing into the air mass. The “volume” of the air mass cannot be assigned any specific numerical value.

2. Holding Variables Constant: The second major reason for the inapplicability of many gas laws to the free atmosphere is that they often require one or more atmospheric variables to be held constant while a second variable is moved or allowed to move over a range of values. This is simply not possible in the free atmosphere. Consequently, no gas law that requires one or more variables to be kept constant may be applied to the free atmosphere.

As a general rule, whenever a mass of air moves across a landscape, all three of the major parameters of the atmosphere (pressure, density, and temperature) can be expected to vary significantly—and not necessarily in fixed relationships to one another.

3. Conditions of Equilibrium: The third major reason why many gas laws fail in dealing with the realities of a dynamic free atmosphere is that they require that a [condition of equilibrium](#) exist—if not actually during the experiment, then at its beginning and at its end. The free atmosphere is—for all intents and purposes—rarely in a condition of equilibrium. Therefore, laws and equations that require a condition of equilibrium have limited applicability to the dynamic free atmosphere.

If we take any significant portion of the free atmosphere, it is first of all subject to the earth's gravitational field, and secondly involved in rotating about the earth's axis. It is almost certainly being either warmed or cooled, with photons being emitted and being absorbed. It most likely will be having water vapor added to it or condensing out of it—even if these processes are not visible. Finally, it will probably be in motion relative to the earth's surface. None of these things are compatible with conditions of equilibrium.

Having gone this far, let us examine some specific gas laws in terms of how they apply or do not apply to atmospheric processes in the free and dynamic atmosphere. Many of these laws are precursors to and are subsumed in the *Ideal Gas Equation of State*. Consequently, in some cases, I have taken the liberty of paraphrasing them in terms of that equation.

I have also changed the notation to keep it in accordance with the notation used in the rest of these essays. In particular, P and p become \bar{p} ; and T becomes \bar{T} . In both kinetic gas theory and statistical mechanics, it is important to keep in mind that these parameters represent mean values of populations that display a wide range of individual molecular and subsystem values.

Amonton's Law: Amonton invented a thermometer in the middle 1600's that used the relationships between the temperatures and the pressures of a fixed volume of gas. He found that:

$$\bar{p}_1\bar{T}_2 = \bar{p}_2\bar{T}_1 \text{ (volume kept constant)} \quad \text{GLF01}$$

Since there was no available temperature scale at that time, his thermometer could not be calibrated for universal use. It is interesting to note, however, that this relationship is a linear one, and therefore implies the existence of absolute zero.

Amonton's Law is **not applicable** to the free atmosphere because it is impossible to maintain a constant volume of the free atmosphere. If you maintain a constant volume, it is no longer free.

Avogadro's Law: In its simplest form, Avogadro's Law is a mathematical identity. It states that a mole of any substance contains the same number of molecules as a mole of any other substance. In this form, it is indisputable, and applies to gases of the free atmosphere as well as to any other gases—whether they are under conditions of equilibrium or conditions of non-equilibrium. The number of molecules in a mole is often referred to as the *Avogadro constant*, and is:

$$N_A = 6.022140857 \times 10^{23} \text{ molecules per gram-mole}$$

with an additional three orders of magnitude for the kilogram-mole.

However, when expressed in terms of the *Ideal Gas Equation of State*, it is usually put into the form that, **for any given combination of temperature and pressure, the number of molecules per unit volume is the same for any gas or any combination of non-reacting gases:**

$$\bar{n} = \frac{\bar{p}}{k_B \bar{T}} \quad \text{GLF02}$$

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

Avogadro's Identity is valid only under the same conditions of equilibrium that normally apply to the Ideal Gas Equation of State. Specifically, it is not valid when the air is in net movement—unless, that is, the manometer measuring the pressure is itself drifting with the wind.

The Barometric Formula: This formula assumes that the pressure at elevation z bears a fixed mathematical relationship to the pressure at base level. It is often expressed:

$$\bar{p}_z = \bar{p}_0 \exp\left(-\frac{mgz}{k_B T}\right) \quad \text{GLF03}$$

Here, \bar{p}_z is the pressure at elevation z , \bar{p}_0 is the pressure at base level, m is the singular molecular mass, g is the singular gravitational constant, k_B is Boltzmann's Constant, and T is the singular temperature in Kelvins.

The Barometric Formula is **not applicable** to the free dynamic atmosphere. It assumes that the atmospheric is isothermal from top to bottom, that the mean molecular mass is constant throughout, that the gravitational constant is uniform throughout, that the atmosphere is in a state of equilibrium, and—finally—that the mass of the overlying air is represented by a column, rather than by a conic or pyramidal section. None of these assumptions are true. Moreover, during significant weather events, the distribution of pressure with elevation usually departs radically from this projection.

Bernoulli's Law: Bernoulli showed that **the flow of any fluid (including air) across a surface creates a change in fluid pressure on that surface**. When that flow is parallel to a surface (real or imaginary) the pressure drops in proportion to the square of the fluid velocity. For the atmosphere, the relationship is:

$$\Delta\bar{p} \propto -\frac{1}{2}\bar{n}\bar{m}\bar{\omega}^2 \propto -\frac{1}{2}\bar{\rho}\bar{\omega}^2 \quad \text{GLF04}$$

Here, $\Delta\bar{p}$ is the change in mean pressure on the surface in Pascals, \bar{n} is the mean number of molecules per cubic meter, \bar{m} is the mean molecular mass in kilograms, $\bar{\rho}$ is the mean mass density in kilograms per cubic meter, and $\bar{\omega}$ is the wind velocity in meters per second. Note the use of the proportional sign rather than the equal sign. Similar equations describe the pressure change for surfaces whose orientation is other than parallel to the flow.

Bernoulli's Law is **applicable** to the free atmosphere, and **must** be applied to understand how ambient atmospheric pressures change when the wind blows.

Boyle's/Mariotte's Law: This law may be expressed in a variety of ways. Let's try this one: **If the temperature of a gas is kept constant, then the pressure is inversely proportional to the volume.** Or, mathematically:

$$\bar{p} = \frac{k}{V} \quad (\bar{T} \text{ kept constant}) \quad \text{GLF05}$$

Here, \bar{p} is the mean gas pressure in Pascals, V is the total volume in cubic meters, \bar{T} is the mean gas temperature in Kelvins, and k is a constant of proportionality.

Boyle's Law is **not applicable** to processes in the free atmosphere because it requires both that the mass of air in the free atmosphere have a specific volume and that the temperature must somehow be maintained at a constant value.

Charles'/Gay-Lussac's Law: This law may be expressed as: **If the pressure of a gas is kept constant, then the volume is inversely proportional to the temperature.**

$$V = \frac{k}{\bar{p}} \quad (\bar{T} \text{ kept constant}) \quad \text{GLF06}$$

Here, all the terms retain their previously assigned denotations.

Charles' Law is **not applicable** to processes in the free atmosphere because it requires both that the mass of air in the free atmosphere have a specific volume and that the pressure must somehow be maintained at a constant value. In all fairness, it should be noted that much heating and cooling of parcels of air takes place under conditions that are very close to isobaric. Segregating out a specific volume is another matter.

Dalton's Law of Partial Pressures: This law may be expressed as: **The pressure of a mixture of non-reacting gases is equal to the sum of their individual partial pressures.** That is,

$$\bar{p}_{abc} = \bar{p}_a + \bar{p}_b + \bar{p}_c \quad \text{GLF07}$$

An interesting logical consequence of this law is that, in essence, every non-reacting gas behaves as if no other gas were present.

Dalton's Law of Partial Pressure is **applicable** to the free atmosphere as long, and only as long, as the air is not moving with respect to the manometer.

Graham's Law of Diffusion: Graham found that **the rate at which gases diffuse is proportional to the square-root of their molecular masses**. Since the kinetic energy of translation is the product of the mass and the mean square of the component speeds, it would appear that some measure of molecular speed is actually at work. A moment's thought leads us to conclude that this rate of diffusion is a function of the mean speed at which gas molecules pass through a plane surface. That speed is the [mean impulse speed](#):

$$\bar{v}_i = \left(\frac{\pi k_B \bar{T}}{2 \bar{m}_i} \right)^{\frac{1}{2}} \quad \text{GLF08}$$

Here, \bar{v}_i is the mean velocity normal to the plane of that selected set of molecules actually passing through the plane in some measure of time, k_B is Boltzmann's Constant, \bar{T} is the mean molecular temperature, and \bar{m}_i is the mean molecular [impulse mass](#) of that subset of molecules.

Graham's Law **is applicable** to the free atmosphere when it is still; and **is not applicable** when the air is in motion. Under the latter conditions, turbulent mixing far overwhelms simple diffusion.

Ideal Gas Equilibrium Equation of State (Laboratory Version): This equation relates the parameters of an ideal gas under conditions of equilibrium. Indeed, an Ideal Gas is defined as one that is completely described by the Equation of State.

$$\bar{p}V = R\bar{T} \quad \text{GLF09}$$

Here, \bar{p} is the pressure in Pascals, V is the volume of one mole of the gas in cubic meters, R is the universal gas constant in joules per mole, and \bar{T} is the absolute temperature in Kelvins.

The term R is actually Avogadro's Number times Boltzmann's Constant. Consequently it has the value:

$$R = 8.3148598 \times 10^3 \text{ Joules per kg-mole per Kelvin}$$

This version of the Ideal Gas Equation of State is **not applicable** to processes in the free atmosphere because it requires both that the mass of air in the free atmosphere have a specific volume and that the number of molecules in the mass of air is somehow maintained at a constant value.

Ideal Gas Equilibrium Equation of State (Thermodynamic Version): In thermodynamics, the Ideal Gas Equation of State may be expressed as:

$$\bar{p} = \bar{n}k_B\bar{T} \quad \text{GLF10}$$

Here, \bar{p} is the mean gas pressure in Pascals, \bar{n} is the mean number of gas molecules per cubic meter, k_B is Boltzmann's Constant in joules per molecule per degree, and \bar{T} is the mean molecular temperature in Kelvins. The combination $k_B\bar{T}$ is often call the *thermal term*.

The thermodynamic version of the ideal gas equation of state is **not applicable** to parcels of air in motion or in any system where weather is occurring.

Ideal Gas Equilibrium Equation of State (Kinetic Version): In kinetic gas theory, the Ideal Gas Equation of State may be expressed as:

$$\bar{p} = \bar{n}\bar{m}_i\sigma^2 \quad \text{GLF11}$$

Here, \bar{p} is the mean gas pressure in Pascals, \bar{n} is the mean number of molecules per cubic meter, \bar{m}_i is the mean molecular impulse mass in kilograms, and σ^2 is the mean of the squares of the axial molecular velocities.

The kinetic version of the ideal gas equation of is **not applicable** to parcels of air in motion or in any system where weather is occurring.

Van der Waal's Equation: This last of the major gas laws to be discovered postulates that **at low temperatures and high densities, forces exist between molecules that both attract and repel them**. This is usually expressed as:

$$\left(\bar{p} + \frac{a}{V^2}\right)(V - b) = R\bar{T} \quad \text{GLF12}$$

Here, a and b are coefficients that vary with the nature of the gas, and the other terms have their previously defined meanings. At normally-occurring temperatures and pressures, a and b approach zero, and the equation becomes:

$$\bar{p}V = R\bar{T} \quad \text{GLF09}$$

the Ideal Gas Equilibrium Equation of State.

Van der Waal's Equation is **valid for the free atmosphere**, and becomes particularly applicable when dealing with evaporation and condensation phenomena.

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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