# HEAT AND TEMPERATURE:  DEFINITIONS OF TERMS

## Introduction

Students of classical thermodynamics often have trouble with atmospheric thermodynamics—and rightfully so.  Classical thermodynamics is largely a laboratory science based on experimentation with fixed quantities under controlled conditions.  Atmospheric thermodynamics is almost entirely an observational science based on indeterminate quantities under uncontrolled conditions in the free atmosphere.

Before undertaking observations in the free atmosphere, there are several points to keep in mind:

**1. Atmospheric systems are open systems.**  They are neither isolated nor closed.  There are continuous interchanges of both matter and energy between atmospheric systems and their environments.

**2. Both system masses (M) and system volumes (V) are indeterminate.**  Both the spatial boundaries and the temporal boundaries of atmospheric systems are vague and ill-defined.  Atmospheric systems are not separate from their environments, but are vigorously mingling and interacting with them.  Expressions that assign a unique value to either system mass or system volume have limited applicability.

**3.  Within any atmospheric system, the values for pressure ($\bar{p}_i$), temperature ($\bar{T}$), and molecular number density ($\bar{n}$) are continuously changing.**  This change is from place to place within the system at any given instant, and from time to time at any given location.  This is why these variable as shown as means (bar over parameter designation) rather than specific values.

**4. Atmospheric systems all contain water vapor.**  Most weather systems contain liquid water and/or solid water (ice) as well.  Since the triple-point for water (273.16K) is well within the normal range of atmospheric temperatures, changes of phase are common occurrences in atmospheric systems.   Hence, observations based on the behavior of dry air under laboratory conditions are of limited value.

**5. Atmospheric systems are non-equilibrium systems.**  Equations and other expressions that require equilibrium conditions to be valid should be avoided.  The Ideal Gas Equation (PV=nRT) is not valid when applied to atmospheric systems in the free atmosphere.  This is not because the gases of the atmosphere are not ideal gases (they aren't, but often behave as if they were); but because the equation requires conditions of equilibrium to be valid and real atmospheric systems are never in a condition of equilibrium.

## Definitions

**Absolute Zero**—the theoretical minimum point on any temperature scale.  For the Kelvin scale, this point is 0K.  For the Celsius scale, it is -273.15°C.  For the Fahrenheit scale, it is -459.67°F.  A system at absolute zero has some minimal molecular motions, and thus still has some remaining energy—the zero-point energy—as required by quantum thermodynamics.

Since no system in the free atmosphere even comes close to absolute zero, the concept is interesting; but has little value except to remind us that our temperature scales are absolute and not relative.

**Conduction**—involves molecule to molecule "contact".  During such contact, the molecules are presumed to exchange kinetic energies much in the same way as colliding billiard balls.  Because air is an extremely poor conductor (and a good insulator) of heat.  Conduction plays only a minor (about 4%) role in the atmosphere's heat budget.

**Degrees of Freedom**—denote the number of possible ways in which a distribution of molecules may allocate their thermal energy.  This number is a function of the temperature of the system and of the atomic configurations of the constituent molecules.

**Monatomic molecules** (like argon, neon, krypton, etc.) have three possible degrees of freedom—all of them involving kinetic energies of translation along the three possible axes of translatory motion.  Under the range of temperatures usually found in the free atmosphere, all three of these degrees of freedom will be activated.  Monatomic molecules are presumed to have no degrees of freedom of either rotation or vibration/libration.

**Diatomic molecules** (like nitrogen and oxygen) have three degrees of freedom of translation and two degrees of freedom of rotation.  The third degree of freedom (about the common axis) is presumed to be physically meaningless.  Diatomic molecules may also possess up to one degree of freedom of vibration and one of libration.  At the temperatures normally encountered in the free atmosphere, none of the common atmospheric diatomic gases possess any measureable degree of vibrational/librational activity.

**Polyatomic molecules** (like water vapor, carbon dioxide, methane, etc.) can have three degrees of translational freedom, up to three degrees of rotational freedom (two, if they are linear molecules), and one degree of vibrational freedom and one degree of librational freedom for each interatomic bond.  Most of these polyatomic atmospheric molecules have some measure of vibrational/librational activity.  Hence, they play significant roles (especially water vapor) in the Earth's heat budget.

Although each molecular configuration has a fixed number of possible degrees of freedom—not all of these degrees need to be fully activated at a given system temperature.  This means that—out of the entire population of molecules---some molecules may be activated and some not.  This results in a fractional degree of freedom for the molecular population for that mode.  For instance, at 25°C water vapor has 6.076 degrees of freedom:  three of translation, three of rotation (the water vapor molecule is non-linear), and 0.076 of vibration/libration.

THE KINETIC ATMOSPHERE
Heat and Temperature:  Definitions of Terms

Keep in mind that, for a mole of water vapor, some $4.57 \times 10^{22}$ molecules will be activated at that temperature.  This is a very large number even though it is a very small percentage.  It is easily possible for a significant number of molecules in a volume of humid air to be activated without that additional specific heat ever showing up in the measurements.

**Electromagnetic Radiation**—is the chief method by which thermal energy is transferred from the Sun to the global Earth, within the Earth-Atmosphere system, and from the global Earth into space.   This series of papers uses the quantum view, which treats electromagnetic radiation as the emission, transfer, and absorption of photons.

For our purposes, we will assume that a photon is emitted when a molecule moves from a higher energy state to a lower one.  The photon does not exist prior to that occurrence. The energy content ($h\nu$) of the emitted photon is exactly equal to the drop in molecular energy.  Conversely, when a photon is absorbed by a molecule, the photon ceases to exist.  Instead, the molecule moves from a lower energy level to a higher one.  Again, the gain in the molecular energy is exactly equal to the energy content of the absorbed photon.

**Enthalpy**—is a measure of the total kinetic energy of all modes of a closed system ($U = u_i^{\Sigma}$) plus an allowance for the total potential energy ($\bar{p}_i V$) of that system. The result is the enthalpy ($H$) of that closed system:  $H = U + \bar{p}V$.

Since neither the global atmosphere nor any of its component systems are closed; and since no system of the free atmosphere has a fixed volume, the concept of enthalpy is undefined for atmospheric systems.

**Entropy**—is a measure of the degree of randomness of molecular behavior in a system.  When a system is in equilibrium, its entropy is maximized.  Since no atmospheric system is in a condition of equilibrium, the entropy of any atmospheric system is always capable of increase.  This is usually done by simple

expansion (spatial diffusion) of the system—either thermal expansion or adiabatic expansion.  Both occurrences are very common in atmospheric systems.

**Equivalence of Phase Temperatures**—is the principle that if two or more phases of the same substance (water vapor, water, and ice—for instance) have the same temperature, then the transfer of the total kinetic energy of all modes across the phase interface is the same in both directions; i. e.,

$$\bar{T} = \frac{\bar{u}_{vapor}^{\Sigma}}{\mathbf{k_B}} = \frac{\bar{u}_{liquid}^{\Sigma}}{\mathbf{k_B}} = \frac{\bar{u}_{solid}^{\Sigma}}{\mathbf{k_B}}$$

This equivalence is required by the *Zeroeth Law of Thermodynamics*.

**Heat:  Classical Thermodynamics**—those forms of energy that are transferred from a hotter substance to a cooler one solely because of the difference in temperature between the two substances.  There is no transfer of heat from a cooler substance to a warmer one.  If the two substances are the same temperature, there is no transfer of heat.  If the transfer of energy is caused by anything other than the difference in temperature, it is not a transfer of heat.

**Heat:  Common Usage**—any form of energy transfer that produces a sensation of warmth.

**Heat:  Engineering**—generally the same as thermal energy.  In engineering the quantity of heat produced by a heat source is independent of the temperature of any heat sink involved.

**Heat Transfer**—involves the transfer of heat from one system to another.  There are three possible ways of doing this:  electromagnetic radiation, conduction, and mass transfer.

THE KINETIC ATMOSPHERE
Heat and Temperature:  Definitions of Terms

**Kinetic energy of libration**—the energy involved in any rhythmic variation in the intramolecular bonding angles.  This energy is often grouped with kinetic energy of vibration, because both involve rhythmic movements.  There are three different modes of kinetic energy of libration possible between any two atoms of a molecule, but a single degree of freedom for each interatomic bond.

**Kinetic energy of rotation**—the energy involved in the rotation of a molecule about one or more of its three axes.   Monatomic molecules have no rotational degrees of freedom.  Diatomic molecules have two degrees of rotational freedom.  The third—rotation around the common axis—is considered to have no physical reality.  Polyatomic molecules may have either two degrees of rotational freedom if they have a common axis, or three degrees of rotational freedom if they do not.  At the temperatures normally encountered in the free atmosphere, not all of the rotational degrees of freedom need to be fully activated.

**Kinetic energy of translation**—the energy involved in any movement of a molecule from one place to another.  There are three degrees of freedom of translation, corresponding to movements along the three dimensions of physical space.  We may assume that all atmospheric gas molecules activate all three translational degrees of freedom.

**Kinetic energy of vibration**—a rhythmic variation in the intramolecular bonding distances.  This energy is often grouped with kinetic energy of libration, because both involve rhythmic movements.  There are three different modes of kinetic energy of vibration possible between any two atoms of a molecule, but they are grouped into a single degree of freedom for each interatomic bond.

**Mass Transfer of Thermal Energy**—is the second (after electromagnetic radiation) most important mechanism for the transfer of thermal energy within both the Earth's atmosphere and its oceans.  Modes of mass transfer involve winds,

water currents, evaporation, condensation, precipitation and every other way in which molecules move from one place to another.

All such mass transfers are three-dimensional, hence I avoid such two-dimensional concepts as advection and convection as unnecessarily limiting.  This principle is readily accepted in Oceanography but seems to be resisted in Meteorology, with its traditional reliance on two-dimensional wind measurement devices.

**Photons**—are the quantized units of electromagnetic radiation.  They are viewed as massless particles traveling at the speed of light ($c$).  As they travel, they alternate rhythmically between electromagnetic and electrostatic modes.  The distance that they travel in one complete cycle is called the wavelength ($\lambda$) of that photon.  The frequency ($v$) is the number complete cycles per second.  The rigorous relationship between these three parameters is: $\lambda v = c$.  That is, the wavelength times the frequency is equal to the speed of light.

The energy content of each photon is directly and rigorously related to its frequency and wavelength.  This energy is expressed as:

$$e = hv = h\frac{c}{\lambda}$$

Here $e$ is the energy content of the photon and **h** is Planck's constant.  Note that high energy photons have short wavelengths and high frequencies.  Low energy photons have long wavelengths and low frequencies.

**Photon Absorption and Emission**—the essence of quantum thermodynamics is that the photons emitted by a substance or absorbed by it have rigorously set values.  Each different molecular configuration—including isotopes, ions and polymers—has a different and very precise set of wavelengths at which it may either absorb or emit photons.  This set (the spectrum of that substance) may be quite large, but it is not infinite.

THE KINETIC ATMOSPHERE
Heat and Temperature:  Definitions of Terms

(For those of you who are not physical scientists, it is axiomatic that if a substance is capable of absorbing photons of a specific wavelength or frequency or energy level, then it is also capable of emitting photons of that identical wavelength or frequency or energy level if conditions are right.)

No substance may absorb or emit photons of any wavelength not included in its spectrum under any conditions.  This characteristic of matter is the foundation of spectrographic analysis.  By examining the wavelengths that a substance emits or absorbs, we may ascertain its chemical composition.

It should be noted that individual substances may share segments of their spectra.  That is, both substances may absorb and emit at one or more particular wavelengths.  However, their overall spectra will be different.  For example, both water vapor and carbon dioxide gases absorb and emit at some of the same wavelengths, but not at others.  Each of these two atmospheric gases has its own specific spectral signatures.

Liquids and solids present special cases.  In gases, the molecules are discrete entities as they move about.  They only come into "contact" with one another during their frequent collisions.  In liquids and solids, the molecules are in close contact with many other molecules, and are sometimes bonded to them in certain ways.

In terms of quantum thermodynamics, these bonds mean that liquids and solids possess many, many more possible energy levels.  Consequently, the spectra of liquids and solids present virtually continuous bands.  The individual energy levels are present in these bands, but our current technology is incapable of readily distinguishing them.  For this and other reasons, solids and liquids are usually converted into gases before spectrographic analysis is attempted.

**Quantum Mechanics**—is an extremely complex view of physics that includes the hypothesis that all of the fundamental dimensions of physics (mass, distance, time) exist only as whole-number multiples of certain basic minimum quantities—the quantum units for those dimensions.  Physical continua of any kind do not exist.

Time is a finite series of individual quanta of time—individual separated instants—and not a continuous flow.  Distance is a finite series of individual "jumps" and not a continuous line.  Similarly, mass is composed of a collection of individual quanta of matter, beyond which matter is indivisible.  You can have whole-number multiples of any of these quanta, but fractional or decimal amounts simply do not exist in the real world.  They are imaginary products of our limited senses and techniques.

The corollary to this quantization of basic dimensions is that products of these dimensions, such as energy ($ML^2T^{-2}$) are similarly quantized.  Indeed, it was the obvious quantization of energy that led to the development of quantum mechanics.

**Second Law of Thermodynamics**—states that the entropy of the known universe is continually increasing.  Similarly, the entropy of an isolated system cannot decrease.  If the entropy of a closed system decreases, then the total entropy of that system plus its environment must increase by an amount at least as great as the entropy decrease of the closed system.  Like time, entropy has an arrow and it goes in only one direction—towards increasing entropy.

**Specific Heat**—in closed systems (which atmospheric systems are not), this is the amount of heat necessary to warm a mole of a substance by one Celsius degree under controlled conditions.  These controlled conditions can be either constant pressure (designated as $C_P$) or constant volume (designated as $C_V$).  To get the specific heat per molecule, simply divide the molar specific heat by Avogadro's Number.

In atmospheric systems, the addition of heat to the system results in an increase in the mean kinetic energy of the system.  This, in turn, usually results in an increase both in the temperature of the system and in the increased dispersion of its component gaseous molecules through system expansion and molecular diffusion.  This increased molecular dispersion, of course, may be viewed as an increase in the entropy of the system.

**Temperature: General**—the mean total of all molecular kinetic energies measured along a single axial arm that is normal to and toward the thermometric sensor.

$$\bar{T} = \frac{\bar{u}_i^{\Sigma}}{\mathbf{k_B}}$$

Here, $\bar{T}$ is the temperature in Kelvins, $\bar{u}$ is the mean molecular kinetic energy per molecule, the subscript $i$ indicates that only the molecules that actually interact with the sensing surface during one second of time are being measured and that the measurement is along that single axial arm that is normal to and toward the sensor, the superscript $\Sigma$ indicates that the total of all four (translation, rotation, vibration, and libration) molecular kinetic energies are being measured, and $\mathbf{k_B}$ is Boltzmann's Constant in joules per molecule per Kelvin.

**Temperature: Atmospheric Gases**—in the common dry atmospheric gases (nitrogen, oxygen, and argon), the kinetic energies involved are almost entirely translational and rotational. For diatomic and monatomic gases, the minimum quantum energy jump required for significant levels of vibrational energies requires higher temperatures than are normally found in the free atmosphere.

In contrast, in atmospheric **water vapor** (which is triatomic), up to two percent of the total kinetic energy can be intramolecular vibrational and/or librational at temperatures normally encountered in the free atmosphere. Hence, atmospheric water vapor's ability to absorb and radiate longwave electromagnetic radiation. The remaining (up to 98%) molecular kinetic energies are divided equally between kinetic energies of translation and rotation of the whole molecule.

In atmospheric **carbon dioxide** ($CO_2$), there are the expected three degrees of translational energy of the whole molecule, but only two of rotational energy of the whole molecule. The carbon dioxide molecule is linear (O-C-O), and the third degree of rotation about the molecular axis cannot acquire the minimum quantum energy value without thermal disassociation of the molecule. Carbon dioxide also has two intramolecular vibrational modes and two intramolecular librational

modes.  These involve rhythmic movements of the two oxygen atoms about the central carbon atom.  These vibration/libration modes explain carbon dioxide's substantial longwave absorption/emission spectrum.

The **other polyatomic "greenhouse" gases** display similar properties.  In general the more atoms a molecule has, the more degrees of intramolecular vibration and/or libration are possible; and the greater the capability that molecule has of absorbing and emitting longwave electromagnetic radiation.

**<u>Temperature:  Atmospheric Liquids</u>**—in liquid water, at the temperatures normally encountered in the free atmosphere, all four of the kinetic energies are present, although the kinetic energies of vibration and libration are present in only a small proportion of the water molecules.  The water molecule is non-linear, and thus possesses three degrees of freedom of both molecular translational and molecular rotational kinetic energies.  The proportion of intermolecular vibrational/librational kinetic energies, however, is sufficient for liquid water to absorb and radiate significant amounts of solar and atmospheric longwave electromagnetic radiation.

**<u>Temperature:  Atmospheric Solids</u>**—in ice and other atmospheric solids, virtually all of the thermal energies appear as kinetic energies of vibration and libration.  In ice, both intermolecular and intramolecular vibrations and librations are involved, with intermolecular vibrations and librations dominant.  Starting at about -73°C, rotational energies of the whole ice molecule begin to appear, and increase as the temperature nears the melting point.  Kinetic energies of translation are also present, but at very low levels.

**<u>Thermal Energy</u>**—any and all forms of energy whose gain or loss is capable of producing a change in temperature.  The most common types of thermal energies are the energies of electromagnetic radiation (including electronic energies) and the four molecular kinetic energies; i. e., translation, rotation, vibration, and libration.

It should be noted that most of the thermal kinetic energies of translation and rotation involve the whole molecule, whereas most of the kinetic energies of vibration and libration are intramolecular and involve interatomic bonding distances and angles.  The exception, of course, involves solids.  Here, intermolecular vibrations and librations exceed intramolecular for most common atmospheric solids at most common atmospheric temperatures.

**Thermal Equilibrium**—a situation where two systems interchange equal amounts of thermal energy.  Hence, by the Zeroeth Law of Thermodynamics, the situation where the two systems have the same temperature.

**Work**—is the form of energy involved in moving mass from one place to another.  Mathematically, it is the product of force and mass displacement.  Like other forms of energy, it is measured in Joules.  In the atmospheric sciences, winds, ocean currents, evaporation, condensation, and precipitation all involve work in that mass is moved from one place to another.

**Zeroth Law of Thermodynamics**—the principle that, if two systems are in thermal equilibrium with a third system (a thermometer, for instance), then they are in thermal equilibrium with one another.

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